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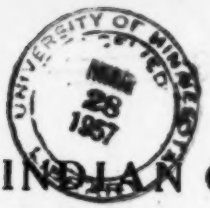

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[Jour. Indian Chem. Soc., Vol 33, No. 12, 1956]

TERPENOIDS. PART II. THE SYNTHESIS OF *dl*-PULEGONE*

By S. M. Mukherji, R. P. Gandhi and O. P. Vig

Starting from 2-carbethoxy-5-methyl*cyclo*hexanone, *dl*-pulegone has been synthesised by taking advantage of Salmi's method of protecting the keto group.

Pulegone, a pleasant smelling camphoraceous oil, is found somewhat widely distributed in nature (Simonsen, "The Terpenes", Cambridge University Press, 1947, Vol. I, p. 371). On the basis of degradative studies, Semmler (*Ber.*, 1892, **25**, 3519) suggested the structure (IIIb) for pulegone, which was later corroborated by Wallach (*Annalen*, 1896, **289**, 337). The αβ-unsaturation was confirmed by its ultraviolet absorption spectrum (Naves and Papazian, *Helv. Chim. Acta*, 1942, **25**, 1023, 1046 and references cited therein).

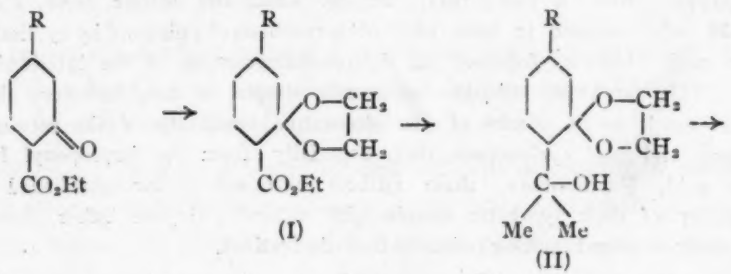
Although Tiemann and Schmidt (*Ber.*, 1896, **29**, 913; 1897, **30**, 22) obtained pulegone from citronellal by the action of acetic anhydride through *iso*pulegol acetate, *iso*pulegol and *iso*pulegone, no direct synthesis was reported till Bardhan and Bhattacharyya (*Chem. & Ind.*, 1951, 800; cf. Kuhn and Schinz, *Helv. Chim. Acta*, 1953, **36**, 161) claimed to have effected a synthesis of pulegone by cyclisation of citronellic acid chloride, followed by dehydrohalogenation of the intermediate chloro-ketone. This synthesis, though apparently simple, is not, however, above scrutiny, in as much as it admits of the alternative possibility of the formation of *cyclo*heptane and / or *cyclo*octane ring, especially from the *iso*propenyl form of citronellic acid. Furthermore, these authors have not so far established the structural identity of their synthetic sample with natural pulegone either through their spectral study or mixed melting points of their derivatives.

We have now worked out a different but simple and unambiguous route which actually constitutes a total synthesis of *dl*-pulegone (IIIb). As pilot experiments, ethyl *cyclo*hexanone-2-carboxylate was treated with ethyleneglycol in presence of *p*-toluenesulphonic acid under the condition prescribed by Salmi (*Ber.*, 1938, **71**, 1803; cf. Surber and Schinz, *Helv. Chim. Acta*, 1954, **37**, 1239) when 2-carbethoxy-*cyclo*hexanone-1-dioxolane (Ia) was obtained in 71% yield. Grignard reaction on this ketal with methylmagnesium iodide afforded a 95% yield of (2-keto-2-dioxolane)-*cyclo*hexyldimethyl carbinol (IIa) which, on decomposition with acid, followed by distillation of the intermediate keto-alcohol (not isolated) with a trace of iodine (cf. Stauffacher and Schinz, *Helv. Chim. Acta*, 1954, **37**, 1239), furnished 2-*iso*propylidene-*cyclo*hexanone (IIIa) in 85% yield. That the double bond in (IIIa) remained exocyclic was checked by its absorption maximum in the ultraviolet region at 252mμ (log ε, 3.66) which is in conformity with the Woodward rule (Fieser and Fieser, "Natural Products related to Phenanthrene", Reinhold, 1949, p. 192) for exo-double bonded αββ-trialkyl-substituted cyclic ketone.

*Since this paper was in the press, a similar synthetic approach to *dl*-pulegone has been reported by Black *et al.* (*J. Chem. Soc.*, 1956, 2971). Their observations are in overall agreement with ours (added in proofs).

Ethyl 5-methyl*cyclo*hexanone-2-carboxylate (Kotz and Hesse, *Annalen*, 1905, **342**, 306) was therefore subjected to the above sequence of reactions when 2-carbethoxy-5-methyl*cyclo*hexanone-1-dioxolane (Ib), (2-keto-2-dioxolane)- *cyclo*hexyl-dimethyl carbinol (IIb) and 2-*iso*propylidene-5-methyl*cyclo*hexanone (IIIb) were obtained in 58%, 95% and 75% yield respectively. The sample (IIIb) showed ultraviolet absorption maximum at 253mμ (log ε, 3.745) in agreement with the value (λ_{max}^{alc}, 253mμ ; log ε, 3.84) recorded by Naves and Papazian (*loc. cit.*) for natural pulegone. Furthermore, these values are in conformity with the Woodward rule.

Both the ketones (IIIa and IIb) furnish deep red 2 : 4-dinitrophenylhydrazones which, though prepared under acidic condition, are assigned to have exo C=C double bond, because under the mild condition employed, the double bond should not migrate into the ring (cf. Frank and Berry, *J. Amer. Chem. Soc.*, 1950, **72**, 2985). Again, the semicarbazone of (IIIb), prepared under mild condition, melts at 169-70° and is therefore formulated as the true semicarbazone and not the carbaminyl pyrazoline derivative which is reported to have m. p. 156-57° (vide Simonsen, *loc. cit.*). Similarly, the derivative obtained from (IIIa) under similar condition was designated as the true semicarbazone.



[a : R=H ; b : R=Me]

*Experimental

*2-Carbethoxy*cyclo*hexanone-1-dioxolane* (Ia).—A mixture of ethyl *cyclo*hexanone-2-carboxylate (50 g.), ethyleneglycol (22 g.), dry benzene (200 c.c.) and *p*-toluene-sulphonic acid (100 mg.) was refluxed in an oil-bath (120°) in a Dean and Stark apparatus till no more water separated. The reaction mixture was neutralised with

*The melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

a little sodium ethoxide and sufficient water was added, and then worked up in the usual way when 45 g. (71%) of the ketal (Ia) distilled over at 120°-124°/8 mm., η_D^{15}, 1.4685. (Found : C, 61.23 ; H, 8.42. $C_{11}H_{18}O_4$ requires C, 61.66 ; H, 8.47 per cent).

(*2-Keto-2-dioxolane*)-cyclo*hexyldimethyl Carbinol* (IIa).—Grignard reagent, prepared from magnesium (4.9 g.) and MeI (30 g.) in dry ether (150 c.c.), was added dropwise to the above ketal-ester (Ia : 21.4 g.) in dry ether (100 c.c.) in the cold. After standing overnight the reaction mixture was decomposed with a saturated solution of ammonium chloride and worked up in the usual manner when the carbinol (IIa : 19 g.) was obtained in 95% yield, b.p. 160-62°/20 mm., η_D^{15}, 1.4753. (Found : C, 65.68; H, 10.23. $C_{11}H_{20}O_3$ requires C, 66.0 ; H, 10.0 per cent).

2-iso*Propylidene*-cyclo*hexanone* (IIIa).—The above ketal-alcohol (IIa : 19 g.) was hydrolysed by heating with a solution of alcohol (25 c.c.), water (240 c.c.) and four drops of HCl (conc.) for 1 hour on the steam-bath. It was then diluted with water and extracted three times with ether. The residue, obtained after removal of the solvent from the combined extract, was distilled with a grain of iodine under 20 mm. pressure, when 11.2 g. (85%) of the unsaturated ketone (IIIa) came over at 120°-125° ; η_D^{20}, 1.4919 ; UV-absorption : $\lambda_{max}^{alc.}$, 252 mμ (log ε, 3.66). (Found : C, 78.03 ; H, 10.31. $C_9H_{14}O$ requires C, 78.21 ; H, 10.14 per cent).

The *2 : 4-dinitrophenylhydrazone*, prepared by the sulphuric acid method in the cold, was crystallised from ethyl acetate as red flakes, m. p. 162-63°. (Found : N, 17.20. $C_{15}H_{18}O_4N_4$ requires N, 17.60 per cent).

The *semicarbazone* was prepared in the usual way and was crystallised from alcohol, m. p. 184°. (Found : N, 21.70. $C_{10}H_{17}ON_3$ requires N, 21.52 per cent).

*2-Carbethoxy-5-methyl*cyclo*hexanone-1-dioxolane* (Ib).—A mixture of 2-carbethoxy-5-methyl*cyclo*hexanone (Kotz and Hesse, *loc. cit.*, 14 g.), ethyleneglycol (10 g.), dry benzene (150 c.c.) and *p*-toluenesulphonic acid (100 mg.) was treated in the same way as in the case of the preparation of (Ia), when 10 g. (58%) of the ketal (Ib) was obtained, b.p. 152-55°/8 mm., η_D^{20}, 1.4653. (Found : C, 62.71 ; H, 8.74. $C_{12}H_{20}O_4$ requires C, 63.13 ; H, 8.77 per cent).

(*2-Keto-2-dioxolane-4-methyl*)-cyclo*hexyldimethyl Carbinol* (IIb).—A solution of the above ketal-ester (Ib : 8.5 g.) in dry ether (50 c.c.) was treated with methylmagnesium iodide (prepared from 1.8 g. of Mg and 12 g. of MeI in 100 c.c. of dry ether) under the same condition as in the case of (Ia). On working up in the usual manner 9 g. (95%) of the desired product (IIb) came over at 132-35°/7 mm., η_D^{20}, 1.4642. (Found : C, 66.97; H, 10.42. $C_{12}H_{22}O_3$ requires C, 67.25; H, 10.28 per cent).

5-Methyl-2-iso*propylidene*-cyclo*hexanone* (IIIb).—The above ketal-alcohol (8.5 g.) was refluxed for an hour with a solution of alcohol (10 c.c.), water (100 c.c.) and two drops of HCl (conc.). After working up in the usual manner, the residue was distilled under reduced pressure with a crystal of iodine, when 4.5 g. (75%) of *dl*-pulegone (IIIb) was obtained, b.p. 101-103°/10 mm., η_D^{20}, 1.4845 (Simonsen, *loc. cit.*, records for *d*-pulegone, b.p. 84°/6 mm., η_D, 1.4846) ; $\lambda_{max}^{alc.}$, 253mμ (log ε, 3.745) (Naves and Papazian, *loc. cit.*, record for *d*-pulegone, $\lambda_{max}^{alc.}$, 253 mμ ; log ε, 3.84). (Found : C, 78.67; H, 10.43. Calc. for $C_{10}H_{16}O$: C, 78.89 ; H, 10.59 per cent).

The 2:4-*dinitrophenylhydrazone*, prepared by the sulphuric acid method in the cold, was crystallised from ethyl acetate as bright red needles, m. p. 142° (Brady, *J. Chem. Soc.*, 1931, 756, reported m.p. 142° for *d*-pulegone derivative). (Found : N, 16.7. Calc. for $C_{16}H_{20}O_4N_4$: N, 16.86 per cent).

The *semicarbazone* was prepared in the usual manner without heating the reaction mixture. On crystallisation from alcohol it melted at 169-70° (Baeyer and Henrich, *Ber.*, 1895, **28**, 653, reported m. p. 172° for the *d*-pulegone derivative). (Found : N, 20.02. Calc. for $C_{12}H_{19}N_3O$: N, 20.08 per cent).

The authors are indebted to Dr. B. K. Bhattacharyya of Jadavpur University, Calcutta for spectral data, and to the National Institute of Sciences of India for the award of a Research Fellowship to one of them (O.P.V.).

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TERPENOIDS. PART III. A NOVEL SYNTHESIS OF *dl*-PHELLANDRAL

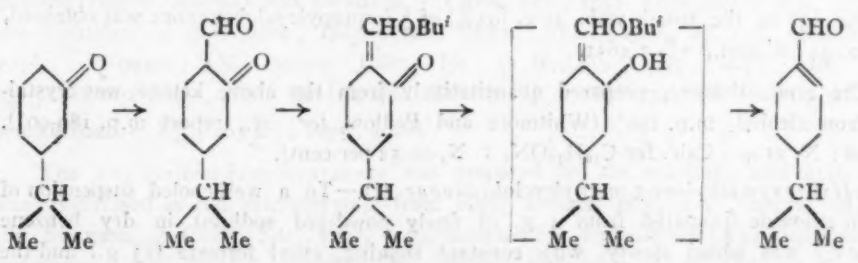
By S. M. Mukherji, T. R. Sharma and O. P. Vig

An elegant new synthesis of *dl*-phellandral has been achieved by adopting the method of Seifert and Schinz for the creation of an $\alpha\beta$-double bond in a *cyclo*hexane aldehyde system.

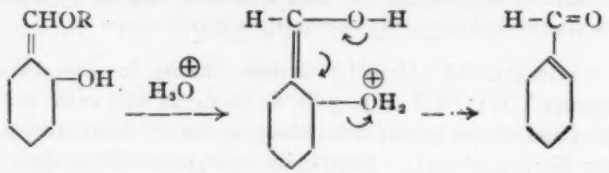
Phellandral, an $\alpha\beta$-unsaturated aldehydic terpene, occurs in several essential oils (Simonsen, "The Terpenes", 1947, Vol. I, p. 308) in *laevo* as well as in *dextro* form. The constitution of phellandral was largely determined by the oxidative studies of Burger and Macbeth (*J. Chem. Soc.*, 1946, 145). Phellandric acid, obtained by silver oxide oxidation of phellandral, followed by hydrogenation, was identified with hexahydrocumic acid (Cooke *et. al.*, *ibid.*, 1940, 808). These authors also synthesised *dl*-phellandric acid by dehydrohalogenation of α-bromohexahydrocumic acid. Frank *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 3889) reported a synthesis of *dl*-phellandral via *dl*-phellandric acid. The latter was resolved by these authors and the *d*-form identified with the optically active acid obtained from the natural *d*-aldehyde. The synthesis by Frank *et al.* (*loc. cit.*), comprising eleven steps, had other limitations as well. For instance, it was difficult to obtain pure phellandric acid which was invariably contaminated with the $\beta\gamma$-isomer. Moreover, the overall yield of phellandral, starting from *p*-cuminol, was very low (about 6%). Recently, another synthesis of *dl*-phellandral has been described by Gillespie *et al.* (*J. Chem. Soc.*, 1955, 665). In this, 1-vinyl-4-*iso*propyl-*cyclo*hexanol was ozonised and the resulting hydroxy-aldehyde, when treated with 2:4-dinitrophenylhydrazone in alcoholic sulphuric acid, underwent dehydration *in situ* to furnish the dinitrophenylhydrazone of *dl*-phellandral from which the aldehyde was regenerated by treatment with pyruvic acid.

We have now evolved a method of synthesis of *dl*-phellandral (IV), which is very much simpler compared to both these methods, and it affords the terpene aldehyde in an overall yield of about 18%, starting from 3-*iso*propyl*cyclo*hex-2-enone. Seifert and Schinz (*Helv. Chim. Acta*, 1951, **34**, 728) prepared 3-methyl*cyclo*hexene-1-aldehyde by lithium aluminium hydride reduction of 2-methyl-6-*iso*butoxymethylene-*cyclo*hexanone, followed by decomposition of the reduced product with a strong acid.

We extended this reaction sequence to 2-*iso*butoxymethylene-5-*iso*propyl*cyclo*-hexanone (II), when a 64% yield of *dl*-phellandral (IV) was obtained.



The decomposition of the reduced product, such as (III), with acid to an unsaturated aldehyde, such as (IV), was explained by Seifert and Schinz (*loc. cit.*) as an anionotropic rearrangement. But as the reaction takes place under strongly acidic condition, this can be explained on the basis of the following sequences as well.



3-*iso*Propyl*cyclo*hexanone, the starting material in the present synthesis, was earlier prepared by Whitmore and Pedlow (*J. Amer. Chem. Soc.*, 1941, **63**, 758) by the action of *iso*propylmagnesium chloride on *cyclo*hex-2-enone. But we preferred a different but more convenient route, comprising catalytic reduction of 3-*iso*propyl-*cyclo*hex-2-enone (Birch and Mukherji, *J. Chem. Soc.*, 1949, 2531) in presence of palladium-charcoal (5%). It was then formylated with ethyl formate under the condition prescribed by Johnson *et al.* (*J. Amer. Chem. Soc.*, 1944, **66**, 218) to obtain the formyl derivative (I). The structure of (I) is based on analogy with carbethoxylation of 3-methyl*cyclo*hexanone (Kötz and Hesse, *Annalen*, 1905, **342**, 306; cf. Part II, this *issue*, p. 853). The formyl derivative (I) was then refluxed with a mixture of *iso*butanol, benzene and a little *p*-toluenesulphonic acid (cf. Seifert and Schinz, *loc. cit.*), when 2-*iso*butoxymethylene-5-*iso*propyl*cyclo*hexanone (II) was produced in 41% yield.

The ultraviolet absorption spectra of the synthetic aldehyde (IV), λ_{max}^{alc}, 229 mμ (log ε, 4.1) and of its semicarbazone, λ_{max}^{alc}, 262 mμ (log ε, 4.34) corresponded with those reported for natural *l*-phellandral by Cooke and Macbeth (*J. Chem. Soc.*, 1938, 1408) and Evans and Gillam (*ibid.*, 1943, 565).

* Experimental

3-iso*Propyl*cyclo*hexanone*.—3-*iso*Propyl*cyclo*hex-2-enone (Birch and Mukherji, (*loc. cit.*) (22 g.) in alcohol (200 c.c.) was shaken under hydrogen in presence of palladium-charcoal (5%, 2.2 g.) till one mole of hydrogen was taken up. After working up in the usual way, 21 g. (95%) of 3-*iso*propyl*cyclo*hexanone was obtained, b. p. 90-94°/8 mm., n_D^{19}, 1.4631.

The *semicarbazone*, prepared quantitatively from the above ketone, was crystallised from alcohol, m.p. 190° (Whitmore and Pedlow, *loc. cit.*, report m.p. 189-90°). (Found : N, 21.4. Calc. for $C_{10}H_{19}ON_3$: N, 21.52 per cent).

2-*Hydroxymethylene-5-methyl*cyclo*hexanone* (I).—To a well-cooled suspension of sodium ethoxide (prepared from 4 g. of finely powdered sodium) in dry benzene (150 c.c.) was added slowly, with constant shaking, ethyl formate (13 g.) and the

* Melting and boiling points are uncorrected. Analyses by Drs. Strauss and Weiler, Oxford.

contents allowed to stand for about 2 hours. 3-*iso*Propyl*cyclo*hexanone (25 g.) in dry benzene (20 c.c.) was then added dropwise with swirling. The reaction mixture was then kept in a refrigerator for 24 hours and the solid mass was decomposed with ice-water. The aqueous layer was separated and acidified with iced HCl. The oily product was twice extracted with ether and the combined ethereal extract washed free of acid. After removal of the solvent the residual oil on distillation under reduced pressure came over at 135°-140°/12 mm., η_D^{16}, 1.4922; yield 21 g. (71%). (Found: C, 71.48; H, 9.71. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59 per cent). It gave an intense violet coloration with alcoholic ferric chloride solution.

2-iso*Butoxymethylene*-5-iso*propyl*cyclo*hexanone* (II).—A mixture of the above hydroxymethylene derivative (I: 20 g.), *iso*butyl alcohol (13.5 g.), dry benzene (125 c.c.) and *p*-toluenesulphonic acid (100 mg.) was refluxed in an oil-bath (120°) under a Dean and Stark water separator till no more water had separated. The cooled reaction mixture was diluted with water and the benzene layer washed with dilute alkali to remove *p*-toluenesulphonic acid and unchanged (I). The organic layer was then dried (Na_2SO_4) and the solvent removed. The residue on distillation yielded 11 g. (41%) of (II), b.p. 185°-190°/8 mm., η_D^{16}, 1.4728. (Found: C, 74.55; H, 11.19. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.78 per cent).

dl-*Phellandral* (IV).—To a suspension of lithium aluminium hydride (1.56 g.) in absolute ether (150 c.c.) was added with mechanical stirring 2-*iso*butoxymethylene-5-methyl*cyclo*hexanone (II: 10 g.) in absolute ether (20 c.c.) at such a rate as to produce a gentle reflux. After the addition the reaction mixture was refluxed for another 15 minutes and then cooled to 10°. To his was then added dropwise, the temperature being kept below 0°, a well-cooled solution of H_2SO_4 (conc., 40 c.c.), ice (30 g.) and water (10 c.c.). Stirring was continued for one hour more and then the reaction mixture was diluted with water and extracted with ether. The ethereal extract, after being washed with sodium bicarbonate and water, was dried (Na_2SO_4) and fractionated when 4.3 g. (64%) of (IV) was obtained, b.p. 110°-115°/7-8 mm. (Found: C, 79.72; H, 10.61. Calc. for $C_{10}H_{16}O$: C, 78.89; H, 10.59 per cent). η_D^{19}, 1.4885 (Frank *et al.*, *loc. cit.*, report η_D^{20} 1.4869); λ_{max}^{alc}, 229 mμ (log ε, 4.1) (Cooke and Macbeth, *loc. cit.*, report for *l*-phellandral, λ_{max}^{alc}, 228.5 mμ; log ε, 4.27).

The *semicarbazone*, prepared in the usual way, crystallised from alcohol, m.p. 203-204° (Berry, Macbeth and Swanson, *J. Chem. Soc.*, 1937, 1448, report m.p. 200° for the *d*-phellandral derivative; Iskenderov, *Chem. Abst.*, 1938, **32**, 126, records m.p. 204°). (Found: N, 20.00. Calc. for $C_{11}H_{19}ON_3$: N, 20.10 per cent). λ_{max}^{alc}, 262 mμ (log ε, 4.34) (Evans and Gillam, *loc. cit.*, reported for *l*-phellandral semicarbazone, λ_{max}^{alc}, 265 mμ; log ε, 4.18).

The 2:4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method and was crystallised as red microcrystals from ethyl acetate, m.p. 204° (Berry, Macbeth and Swanson, *J. Chem. Soc.*, 1937, 1449, reported for *d*-phellandral-2:4-dinitrophenylhydrazone, m.p. 204°). (Found: N, 16.70. Calc. for $C_{16}H_{20}O_4N_4$: N, 16.86 per cent).

The oxime was prepared according to the directions of Fuson and Shriner ("Identification of Organic Compounds", John Wiley, 1948, p. 202) and was crystallised from dilute alcohol, m.p. 87° (Iskenderov, *loc. cit.*, reported m.p. 87.8°). (Found : N, 8.15. Calc. for $C_{10}H_{11}ON$: N, 8.15 per cent).

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STUDIES IN CARBOHYDRATES. PART V. INVESTIGATION OF THE GUM FROM *ACACIA CATECHU*

By R. K. Hulyalkar, T. R. Ingle and B. V. Bhide

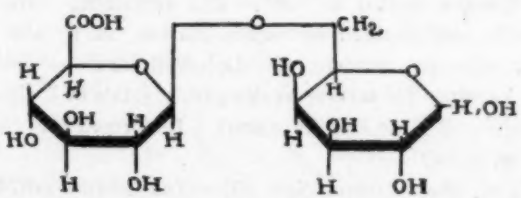
The gum from *acacia catechu* is composed of D-galactose (9 mols.), L-arabinose (4 mols.), D-rhamnose (3 mols.) and L-glucuronic acid (3 mols.). On hydrolysis with 10% sulphuric acid the gum yields an aldobiuronic acid, which is found to be 6-β-D-glucuronosido-D-galactose by using the methylation technique.

Acacia catechu (N. O. Leguminoseae) is widely distributed throughout India. The gum obtained from the tree is regarded as a good substitute for gum arabic. However, it has not been chemically investigated so far.

The gum, as supplied by the Forest Officer, Bombay State, was in the form of nodules and was easily soluble in water, non-reducing and neutral to litmus. It could be precipitated by alcohol from its aqueous solution in the form of a white powder. It did not contain nitrogen, acetyl or methoxyl group. It gave ash (3.1%) which was mainly composed of Fe^{3+}, Ca^{2+}, Mg^{2+} and SO_4^{2-}. The gum acid was obtained almost ash-free by treating the aqueous solution of the crude gum with acidified alcohol.

The acid was non-reducing and had equiv. 1025 (*ca.*), $[\alpha]_D^{27}$,-32° (*c*, 2% in 0.5% NaOH). On hydrolysis with 10% sulphuric acid it afforded L-arabinose, D-galactose, L-rhamnose and an aldobiuronic acid. These sugars were isolated in crystalline forms and their physical properties were studied. Their identity has further been confirmed by preparing their crystalline derivatives. The uronic acid is shown to be D-glucuronic acid by isolating the characteristic crystals of potassium acid saccharate by simultaneous hydrolysis and oxidation of the aldobiuronic acid according to the method of Heidelberger and Goebel (*J. Biol. Chem.*, 1927, **74**, 613).

To elucidate the structure of the aldobiuronic acid, it was fully methylated, initially with sodium hydroxide and dimethyl sulphate, and finally by Purdie's reagent. The fully methylated ester shows η_D^{28} 1.4717 ; $[\alpha]_D^{28}$, -23° (*c*, 0.8% in chloroform). On hydrolysis it yielded 2 : 3 : 4-tri-*O*-methyl-D-galactose and 2 : 3 : 4-tri-*O*-methyl-D-glucuronic acid. These results indicate that the aldobiuronic acid obtained from the gum is 6-β-D-glucuronosyl-D-galactose.



The aldobiuronic acid is thus identical with the one obtained from gum arabic (Challinor, Haworth and Hirst, *J. Chem. Soc.*, 1931, 258).

Experimental

The crude gum gave a viscous solution in water. It was filtered through muslin and was added to alcohol, when the gum was precipitated as a white powder. It formed a neutral solution in water which was non-reducing. The ash content was 3.1%, which gave positive tests for Fe^{3+}, Ca^{2+}, Mg^{2+} and SO_4^{2-}. It did not contain nitrogen, methoxyl or acetyl group.

Purification of the Gum.—The gum (150 g.) was dissolved in a litre of 1% NaOH solution, filtered through cloth, made just acidic to Congo red, and was poured into alcohol (95%, 3 litres), when the gum was precipitated as a white powder. Three similar treatments afforded the gum acid with negligible ash content. It was non-reducing and possessed equiv. of 1025 (*ca.*). It showed positive tests for pentosans, methylpentosans and galactan. The quantitative analysis of the gum by usual methods (cf. Ingle and Bhide, this *Journal*, 1954, **31**, 939) gave galactose (49.9%), arabinose (17.5%), rhamnose (14.0%) and uronic anhydride (17.6%); the figures in each case being calculated for anhydro-sugar units. These results indicate that the polyuronide should be composed of nine units of galactose, four of arabinose, three of rhamnose and three of glucuronic acid. Such a polyuronide should possess an equivalent of 990 and should be composed of galactose (49.08%), arabinose (17.75%), rhamnose (14.75%) and uronic anhydride (17.76%).

Hydrolysis of the Gum by 10% H_2SO_4.—The purified gum (4.8 g.), dissolved in 10% H_2SO_4, was heated on a water-bath at 90°. The hydrolysis was followed by finding out the reducing power of the hydrolysate at different intervals.

Time interval	0.5 hr.	1.5 hr.	4 hrs.	7 hrs.	8 hrs.
% Reducing sugars (in terms of glucose).	29.1	58.2	77	93.7	93.7

On working out the hydrolysate according to the procedure described by Ingle and Bhide (*loc. cit.*), the non-acidic reducing sugars (A) and the barium salt of the uronic acid (B) obtained were examined as follows.

Examination of the Non-acidic Reducing Sugars (*A*).—Chromatographic examination of the sugar syrup (A) indicated the presence of galactose, arabinose and rhamnose. The identity of these sugars was confirmed by running authentic specimens side by side. The sugar mixture was dissolved in ethyl alcohol (90%) and different crops were separated. The first two crops on further crystallisation gave D-galactose, m. p. and mixed m. p 163°; $[\alpha]_D^{27}$, + 82° (*c*, 2% in water). Its α-methylphenylhydrazone melted at 186°. The remaining crops mainly contained L-arabinose, which was purified by crystallisation, m. p. and mixed m.p. 158°; $[\alpha]_D^{27}$, +108° (*c*, 2% in water); its diphenylhydrazone melted at 201°. The mother-liquor on keeping for several weeks gave crystals of L-rhamnose monohydrate, m. p. 96-97°; $[\alpha]_D^{27}$, -8° (*c*, 0.8% in water). It formed the characteristic *p*-bromophenylhydrazone, m. p. 217°.

Examination of the Barium Salt (*B*).—The barium salt, free from non-acidic reducing sugars, had $[\alpha]_D^{27}$, -2° (*c*, 2% in water); Ba, 16.2%. The barium salt of aldobiuronic acid *i.e.*. $C_{24}H_{38}O_{24}Ba$, requires Ba, 16.1%. On further hydrolysis by 10% H_2SO_4, the aldobiuronic acid gave a non acidic reducing sugar which was

identified as galactose chromatographically, but the barium salt obtained was found to contain 16 to 17% Ba, indicating that it was mainly an aldobiuronic acid and the monouronic acid formed had decomposed. Hence, the uronic acid component was identified by the following method (cf. Heidelberger and Goebel, *loc. cit.*).

The barium salt (B) (2 g.) was dissolved in water (20 c.c.) and barium ions were removed by adding a slightly less than the required quantity of N-H_2SO_4. The solution after filtration was diluted by 2N-HBr (50 c.c.) and bromine (0.5 c.c.) was added to it. The solution was refluxed for about 40 hours. It was necessary to replace bromine from time to time. At the end, the liquid did not reduce Fehling's solution. It was concentrated under reduced pressure, treated with Ag_2CO_3, filtered and heated with H_2S, and the filtrate, thus obtained, was concentrated to a small bulk. On keeping for two days, no crystals of mucic acid were obtained, while the crystals of potassium acid saccharate separated when the concentrate was treated with 60% KOH and acetic acid.

Methylation of the Barium Salt of Uronic Acid (B).—The barium salt (B) (25 g.) was methylated by NaOH and dimethyl sulphate four times and the chloroform-soluble methylated acid was fully methylated and esterified by silver oxide and methyl iodide, yield 15 g., OMe, 50.2%. The product, when distilled under reduced pressure, furnished the following fractions. Fraction I, b.p. 140-150°/5 mm., yield 3 g. Fraction II, b. p. 255°-260°/5 mm., yield 8.5 g. Residue, 3.1 g. (which was not further worked out).

Fraction I was a yellowish liquid having OMe, 59.1%, η_D^{28}, 1.4489. It was shown to be methyl ester of 2 : 3 : 4-tri-*O*-methyl methyl-D-glucuronoside by preparing its amide, which crystallised from ethanol-ether, petroleum ether mixture, m. p. 186° ; $[\alpha]_D^{28}$, + 136° (*c*, 0.8% in water) ; N, 5.57%, OMe, 48.5%. The amide of 2 : 3 : 4 tri-*O*-methyl-α-methyl - D - glucuronoside melts at 183° ; $[\alpha]_D^{30}$, + 137.5° (*c*, 0.7% in water) (Smith, *J. Chem. Soc.*, 1939, 1732), N, 5.6%, OMe, 49.8%. The mixed m. p. of this amide and the authentic sample prepared from D-glucuronic acid remained unchanged.

Fraction II was obtained as a viscous syrup having OMe, 52.9% ; equiv. 460 ; η_D^{28}, 1.4717 ; $[\alpha]_D^{28}$, -23° (*c*, 0.8% in chloroform) ; $[\alpha]_D^{28}$, -3°.1 (*c*, 0.9% in water), indicating that it might be the fully methylated methyl ester of 6-β-D-glucuronoside-D-galactose, which requires OMe, 53% ; equiv., 468 ; η_D^{30}, 1.4715 ; $[\alpha]_D^{30}$, -24° (*c*, 2% in chloroform). (Challinor *et al.*, *loc. cit.*). On hydrolysis, the ester yielded (*i*) 2 : 3 : 4-tri-*O*-methyl-D-galactose, identified chromatographically by running the authentic sample side by side, and by preparing its anilide, m.p. and mixed m. p, 165° and (*ii*) 2 : 3 : 4-tri-*O*-methyl-D-glucuronic acid, identified by preparing methyl ester of 2 : 3 : 4-tri-*O*-methylsaccharolactone, m. p. and mixed m. p. 108-109° ; $[\alpha]_D^{28}$, + 90° (*c*, 1% in water). (cf. Parikh, Ingle and Bhide, this *Journal*, 1956, **33**, 127).

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STUDIES IN CARBOHYDRATES. PART VI. COMPOSITION OF THE MUCILAGE FROM SEEDS OF *MIMOSA PUDICA*

By R. K. Hulyalkar, T. R. Ingle and B. V. Bhide

The mucilage from the seeds of *Mimosa pudica* is composed of D-xylose and D-glucuronic acid in the proportion of 5 : 1 molecules. Its periodate oxidation indicates a branched structure.

Mimosa pudica, Linn. (N.O. Mimoseae), commonly known as Lajalu or Lajawanti in Hindi, is found growing abundantly in hotter parts of India. The seeds have some value in Ayurvedic medicine.

The seeds contain a large amount of mucilageneous matter and swell enormously in contact with water. The mucilage is found to be firmly attached to the seeds and and cannot be separated even by hard pressing. The microscopic examination of the swollen seeds reveals that the mucilage is present in a network of fibres, clinging to the seeds. The crude mucilage was extracted with water and the aqueous extract was poured into alcohol, when it was obtained as an ash-coloured powder. It is non-reducing, neutral and does not contain sulphur, nitrogen, methoxyl or acetyl group. It has an ash content of 18.6%, which is composed of Fe^{3+}, Mg^{2+}, Ca^{2+} and SiO_2. An ash-free mucilage was obtained more easily by extracting it from the seeds with 2% NaOH and precipitating it by alcohol containing HCl. It did not respond to tests for galactan and methylpentosan, but gave positive tests for pentosans.

Hydrolysis of the mucilage by 10% sulphuric acid afforded mainly D-xylose, which was obtained in a crystalline form and characterised by preparing its osazone and dimethylacetal of dibenzylidene-D-xylose. Traces of glucose could also be detected chromatographically. The hydrolysate furnished a uronic acid (isolated as the barium salt) which was identified as D-glucuronic acid. No other uronic acid or sugar could be detected on careful chromatographic examination.

The quantitative estimation of different sugars indicates that the mucilage is composed of D-xylose and D-glucuronic acid in the molecular proportion of 5 : 1 respectively. The oxidation of the mucilage by sodium metaperiodate afforded for one equivalent of the mucilage two molecules of formic acid and consumed five molecules of the oxidant. These results indicate that the mucilage possesses a branched structure.

Experimental

Isolation of the Crude Mucilage.—The seeds (500 g.) were kept in contact with water (4 litres) overnight under toluene. The thick mass, thus obtained, was disintegrated in a Waring blender. The extract was squeezed through muslin and added to alcohol (90%) when the mucilage separated as a thick mass. On trituration with absolute alcohol, it was obtained as an ash-coloured powder, yield 45 g. Its aqueous solution was non-reducing and neutral to litmus. It contained 18.6% ash and found to be composed of SiO_2, 64% ; Fe^{3+}, 14% ; Ca^{2+}, 7.9% and Mg^{2+}, 1.4%.

Isolation and Examination of the Pure Mucilage.—The seeds (500 g.) were kept in contact with 2% NaOH solution (4 litres) overnight. The material was squeezed through a fine cloth and the extract was made acidic to Congo red with HCl. It was added to alcohol (8 litres) with stirring when the mucilage separated as a stringy mass. On trituration with absolute alcohol, it was obtained as a dry powder, yield 18.5 g. Two or three similar treatments gave the pure mucilage (yield 15 g., ash 0.1%, mainly Fe^{3+}). Its aqueous solution was non-reducing and acidic to litmus; equiv., 935; $[\alpha]_D^{28}$, + 24° (*c*, 1.5% in 1% NaOH). It did not respond to the mucic acid test for galactan and Rosenthaler's test for methylpentosan, but gave strong phluroglucinol test, orcinol test and aniline acetate test for pentoses (cf. Ingle and Bhide, this *Journal*, 1954, **31**, 939).

Hydrolysis of the Mucilage by 10% H_2SO_4.—The mucilage (4 g.) was suspended in 10% H_2SO_4 (100 c.c.) at room temperature overnight, and heated at 90°. The rate of hydrolysis was followed by estimating the reducing sugars by Bertrand's method. After complete hydrolysis (5 hours), the hydrolysate was worked up in the usual manner (vide Ingle and Bhide, *loc. cit.*) and the non-acidic reducing sugars were obtained as a syrup (A), while the uronic acid was isolated as its barium salt (B).

The Syrup (A).—A chromatographic examination of the syrup indicated the presence of xylose with a trace of glucose. The presence of xylose was further confirmed by obtaining the characteristic boat-shaped crystals of cadmium bromide-cadmium xylonate (Bertrand, *Bull. Soc. chim.*, 1891, *iii*, **5**, 556). D-xylose was obtained in a crystalline form by dissolving the syrup in glacial acetic acid; m.p. and mixed m.p. 142°; $[\alpha]_D^{28}$, + 93°.5 → + 19° (*c*, 0.7% in water). It gave an osazone, m.p. 158° and dimethylacetal of dibenzylidene-D-xylose, m.p. 210° (cf. Breddy and Jones, *J. Chem. Soc.*, 1945, 739).

The Barium Salt (B).—The precipitate of the barium salt (B) was freed from non-acidic reducing sugars by refluxing several times with alcohol. It had Ba, 26.2; $[\alpha]_D^{28}$, +15° (*c*, 1.5% in water). The barium salt of D-glucuronic acid, *i. e.* $C_{12}H_{18}O_{14}Ba$, requires Ba, 26.1%; $[\alpha]_D^{28}$, +15° (*c*, 1.1% in water) (Hirst and Jones, *ibid.*, 1938, 1179). The barium salt was converted into uronic acid and was oxidised by nitric acid. On concentration and keeping, crystals of mucic acid were not obtained. On the other hand, the oxidised product afforded the characteristic crystals of potassium acid saccharate, when treated with 50% KOH and glacial acetic acid in the usual manner.

The quantitative estimation of different sugars in the mucilage furnished pentosans (79.4%) and uronic anhydride (19.5%). These results indicate that the mucilage is composed of D-xylose and D-glucuronic acid in the proportion of 5 : 1 molecules.

Periodate Oxidation of the Mucilage.—The mucilage (0.312 g.), dissolved in water (20 c.c.), was neutralised with *N*/20-NaOH solution (6.66 c.c.), and sodium metaperiodate (20 c.c., 0.3 *M*) was added to it. The mixture was made up to 50 c.c. and kept at 0° in the dark. A portion of the solution (5 c.c.) was withdrawn at different intervals and the amount of formic acid formed, and that of the sodium metaperiodate consumed were determined by usual methods (Whistler and Hickson,

J. Amer. Chem. Soc., 1954, **76**, 1672). The results obtained for one equivalent of the mucilage are recorded below.

TABLE I

Time (in hrs.)	0	4	8	12	16	24
Formic acid formed (*M*)	...	1.9	2.02	2.08	2.09	2.1
$NaIO_4$ consumed (*M*)	...	4.6	4.96	5.05	5.09	5.11

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STUDIES IN FRIEDEL-CRAFTS' ACYLATION. PART II. ACYLATION OF ACETOTOLUIDIDES AND ACETANILIDE

By V. K. Mehta, (Miss) M. J. Sacha and S. R. Patel

Friedel-Crafts' acylation of acetanilide, aceto-*m*-toluidide and aceto-*p*-toluidide has been investigated using several acyl chlorides. Acetanilide and aceto-*m*-toluidide afforded the corresponding *p*-aminoketones, and in case of aceto-*p*-toluidide, the condensation failed

The work described in this paper is an extension of our previous communication (Sacha and Patel, this *Journal*, 1956, **33**, 129).

Kunckell (*Chem. Zentrl.*, 1912, I, 136) reported that Friedel-Crafts' acylation of aceto-*m*-toluidide with chloroacetyl chloride effected substitution, *para* with respect to the amino group. In this paper Friedel-Crafts' acylation of aceto-*m*-toluidide has been reported with other acyl halides and substitution has been found to occur in a similar position, e.g., with acetyl chloride, 4-acetamino-2-methylacetophenone (I) was obtained in good yield. This successful condensation is contrary to the observation made by Kunckell (*Ber. deut. Pharm. Ges.*, 1911, **21**, 419) that the Friedel-Crafts condensation of an anilide derivative would succeed only if the acyl halide is halogenated or its boiling point exceeds 90°. This as well as other condensations reported in this paper has been carried out by heating an anilide derivative, acyl halide and finely powdered anhydrous aluminium chloride in proportions of 1 : 1 : 3 respectively.

The constitution assigned to (I) has been confirmed by hydrolysing it to the corresponding amino-ketone (II), followed by replacement of the amino group by the hydroxy group on adding the diazotised solution of (II) to a boiling H_2SO_4 solution, and proving the identity of the product obtained, viz., 4-hydroxy-2-methylacetophenone, with the known authentic sample obtained on the Fries rearrangement of *m*-cresyl acetate (Skraup and Poller, *Ber.*, 1924, **57**, 2033). In a similar manner the Friedel-Crafts acylation of aceto-*m*-toluidide with benzoyl chloride, *o*-chlorobenzoyl chloride and *p*-nitrobenzoyl chloride has been carried out successfully, and in each case *p*-substitution occurs.

Friedel-Crafts' acylation of acetanilide with benzoyl chloride furnished *p*-aminobenzophenone in 7% yield (vide Baeyer and Villiger, *Ber.*, 1904, **37**, 605, who obtained it on reduction of *p*-nitrobenzophenone). Similarly, on condensation of acetanilide with *o*-chlorobenzoyl chloride and *p*-nitrobenzoyl chloride, 4-acetamino-2′-chlorobenzophenone (III) and 4-acetamino-4′-nitrobenzophenone were obtained respectively in about 20% and 24% yields. In the previous communication (*loc. cit.*) Friedel-Crafts' acetylation of acetanilide (yield 19%) has been reported. It is interesting to note that acetanilide, which affords on nitration, halogenation etc. the corresponding reaction products in excellent yields, affords the amino-ketones in poor yields on its Friedel-Crafts' acylation.

The free base of (III), viz, 4-amino-2′-chlorobenzophenone (IV), has been reported in literature as a product of indefinite constitution (Montagne, *Ber.*, 1916, **49**, 2251) as the author obtained it on reduction of 4-nitro-2′(?)-chlorobenzophenone (V) which he obtained as one of the products of Friedel-Crafts' acylation of chlorobenzene with *p*-nitrobenzoyl chloride. The identity of (IV) with the product obtained by Montagne confirms the constitution assigned by him to (V).

We have studied the acylation of aceto-*p*-toluidide with both acetyl chloride and benzoyl chloride under different sets of experimental conditions, with and without solvents like acetylene tetrachloride and carbon disulphide, and taking different proportions of the reactants, particularly using a very large excess of anhydrous aluminium chloride; but in each case the reaction failed. Kunckell (*Ber.*, 1900, **33**, 2644) has reported that Friedel-Crafts' acylation of aceto-*p*-toluidide with chloroacetyl chloride affords two products, in one the substitution is *ortho* with respect to the amino group while in the other it is *ortho* with respect to the methyl group. We therefore repeated the work of Kunckell and confirmed his results. Friedel-Crafts' acylation of an anilide derivative leading to *ortho*-substitution with respect to the amino group is rare. The only other instance of this type reported so far is Friedel-Crafts' acylation of 4-acetamino-1 : 2-dimethylbenzene with chloroacetyl chloride (Kunckell and Schneider, *J. prakt. Chem.*, 1912, **86**, 429).

Experimental

Friedel-Crafts' Acylation of Aceto-m-toluidide

Acetylation of Aceto-m-toluidide to 2-Methyl-4-acetaminoacetophenone.—To an ice-cooled mixture of aceto-*m*-toluidide (10 g.) and finely powdered anhydrous aluminium chloride (30 g.) acetyl chloride (10 g.) was added in small lots. The reaction mixture after being kept for half an hour at room temperature was heated on a water-bath for 2 hours and decomposed with ice and HCl, when 2-methyl-4-acetaminoacetophenone separated out as a faint yellow solid. It crystallised from hot water as colorless long needles, m. p. 138-39°, yield 5.5 g. (Found : N, 7.4. $C_{11}H_{13}O_2N$ requires N, 7.3 per cent).

2-Methyl-4-aminoacetophenone.—The above acetamino-ketone was hydrolysed by heating it with an excess of dilute HCl on a boiling water-bath. The product obtained crystallised from petrol in pale brown small needles, m. p. 95-96°. (Found : N, 9.5. $C_9H_{11}ON$ requires N, 9.4 per cent).

2-Methyl-4-acetaminobenzoic Acid.—2-Methyl-4-acetaminoacetophenone (2 g.) was oxidised by heating it with 4% $KMnO_4$ solution (200 c.c.) and magnesium sulphate (8 g.). The colorless solution, obtained on filtration of the hot reaction mixture, after concentration was acidified. The product obtained crystallised from boiling water in colorless, shining, small needles, m. p. 222° (decomp.). (Found : N, 7.6 ; equiv., 195.8. $C_{10}H_{11}O_3N$ requires N, 7.2 per cent. Equiv., 193.0). Kunckell (*loc. cit.*) has reported the melting point as 243°. As the melting points did not agree, the constitution assigned to the above amino-ketone had to be proved by another method shown below.

2-Methyl-4-hydroxyacetophenone (p-*acetyl*-m-*cresol*).—2-Methyl-4-aminoacetophenone (2.0 g.) was dissolved in hot 50% solution of H_2SO_4 (10 c.c.) and cooled below 5°. It was then diazotised with sodium nitrite solution (1.0 g. in 3 c.c. water). The diazotised solution was added in small lots to a well-stirred, boiling 50% solution of H_2SO_4 (20 c.c.). The brown solid, which separated out on cooling, crystallised from boiling water as faint brown scales, m. p. 130-31°. It was found to be identical with *p*-acetyl-*m*-cresol obtained as one of the products (non-volatile) on the Fries rearrangement of *m*-cresyl acetate (Skraup and Poller, *loc. cit.*), mixed m. p. remaining undepressed.

Benzoylation of Aceto-m-*toluidide to 2-Methyl-4-aminobenzophenone.*—The reaction was carried out as indicated above, using benzoyl chloride, the quantities of the reactants remaining the same. The product obtained on decomposition of the reaction mixture with ice and HCl after treatment with dilute bicarbonate solution and final washing with cold water remained pasty even on keeping for a long time. It was therefore hydrolysed to 2-methyl-4-aminobenzophenone which crystallised from benzene as yellowish needles, m. p. 141°, yield 10 g. (Found: N, 6.2. Calc. for $C_{14}H_{13}ON$: N, 6.6 per cent).

2-Methyl-4-hydroxybenzophenone (p-*Benzoyl*-m-*cresol*).—The above amino-ketone was diazotised as indicated before and the diazotised solution was gradually heated to 50° on a water-bath, and kept at that temperature for about 15 minutes. The pasty mass obtained on cooling was extracted with dilute NaOH solution. The clear alkali extract was acidified when an oily substance was obtained which on long standing solidified. It crystallised from benzene in small needles, m. p. 128-29°. It was found to be identical with *p*-benzoyl-*m*-cresol, obtained as one of the products (non-volatile) on the Fries rearrangement of *m*-cresyl benzoate (Heller, *Ber*, 1913, **46**, 1503); mixed m.p. remained undepressed. N-*Acetyl derivative*, obtained by heating 2-methyl-4-aminobenzophenone with an excess of acetic anhydride, crystallised from petrol-ether as yellowish white thin plates, m.p. 128-29°. (Found: N, 5.3. $C_{16}H_{15}O_2N$ requires N, 4.4 per cent).

Acylation of Aceto-m-*toluidide using* o-*Chlorobenzoyl Chloride to 2-Methyl-4-amino-2'-chlorobenzophenone.*—The pasty condensation product, obtained by carrying out the reaction as above, was hydrolysed with hot HCl (conc.) and the product obtained crystallised from boiling water as thin yellowish needles, m. p. 98-100°, yield 4 g. (Found: N, 5.5; Cl, 14.6. $C_{14}H_{12}ONCl$ requires N, 5.7; Cl, 14.4 per cent).

Acylation of Aceto-m-*toluidide using* p-*Nitrobenzoyl Chloride to 2-Methyl-4-amino-4'-nitrobenzophenone.*—The condensation was carried out as indicated above and as the product obtained did not solidify, it was hydrolysed to the amino-ketone which crystallised from benzene as dirty yellow granules, m.p. 149-52°, yield 7 g. (Found: N, 9.5. $C_{13}H_{14}O_4N_2$ requires N, 9.4 per cent).

N-*Acetyl derivative* of 2-methyl-4-amino-4'-nitrobenzophenone crystallised from acetone and petrol-ether mixture as pale yellow granules, m. p. 159-61°. (Found: N, 10.7. $C_{14}H_{12}O_3N_2$ requires N, 10.9 per cent).

Friedel-Crafts' Acylation of Acetanilide

Benzoylation of Acetanilide to p-Aminobenzophenone.—The condensation of acetanilide with benzoyl chloride was effected by the method described above. The amino-ketone obtained on hydrolysis of the condensation product crystallised from boiling water as small pinkish white needles, m. p. 124°, yield 1 g. (Found: N, 6.8. Calc. for $C_{13}H_{11}ON$: N, 7.1 per cent). Baeyer and Villiger (*loc. cit.*), who obtained it on reduction of *p*-nitrobenzophenone, recorded the same m. p.

Acylation of Acetanilide with p-Chlorobenzoyl Chloride to 4-Acetamino-2'-chlorobenzophenone.—The product, obtained by the method described above after washing with dilute bicarbonate solution and finally with water, crystallised from boiling water in thin pinkish plates, m. p. 145-47°, yield 4 g. (Found: N, 5.2; Cl, 12.8. $C_{15}H_{12}O_2NCl$ requires N, 5.1; Cl, 13.0 per cent).

4-Amino-2'-chlorobenzophenone, obtained on hydrolysis of the above acetamino-ketone, crystallised from boiling water in small thin needles, m. p. 112°. (Found: N, 5.8; Cl, 15.2. Calc. for $C_{13}H_{10}ONCl$: N, 6.0; Cl, 15.3 per cent). Montagne (*loc. cit.*) records the same m. p.

N-Benzoyl derivative, obtained by treating 4-amino-2'-chlorobenzophenone with an excess of benzoyl chloride in presence of alkali solution, crystallised from acetone and petrol-ether mixture as dirty yellowish powder, m. p. 132-34°. (Found: N, 4.2; Cl, 10.7. $C_{20}H_{14}O_2NCl$ requires N, 4.1; Cl, 10.6 per cent).

Acylation of Acetanilide with p-Nitrobenzoyl Chloride to 4-Acetamino-4'-nitrobenzophenone.—The product obtained by the method described above, after washing with dilute bicarbonate solution and subsequently with water, crystallised from acetone and petrol-ether mixture as a pale yellow powder, m. p. 194-95°, yield 5 g. (Found: N, 9.7. $C_{15}H_{12}O_4N_2$ requires N, 9.9 per cent).

4-Amino-4'-nitrobenzophenone, obtained on hydrolysis of the above acetamino-ketone, crystallised from acetone as a yellow powder, m. p. 180-81°. (Found: N, 11.7. $C_{13}H_{10}O_3N_2$ requires N, 11.6 per cent).

N-Benzoyl derivative of the above amino-ketone crystallised from acetone and petrol-ether mixture as a yellowish powder, m.p. 199-200°. (Found: N, 7.9. $C_{20}H_{14}O_4N_2$ requires N, 8.1 per cent).

Friedel-Crafts' Acylation of Aceto-p-toluidide

The condensation of aceto-*p*-toluidide with both acetyl chloride and benzoyl chloride was attempted under different experimental conditions mentioned in the theoretical; but in each case the reaction failed and the aceto-*p*-toluidide was recovered unchanged.

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REDUCTION OF DICHROMATE BY IODIDE IN PRESENCE OF CHLORIDES AND BROMIDES

By K. Chatterjee and B. P. Gyani

The reduction of $K_2Cr_2O_7$ by KI in sulphuric acid solutions in presence of varying amounts of chloride and bromide ions has been studied potentiometrically. Presence of small quantities of chloride ions (0.03 *M*) does not interfere with the normal course of the reaction, the titration curve showing only one sharp inflexion corresponding to six moles of KI per mole of $K_2Cr_2O_7$. Higher concentrations of chloride ions lead to two inflexions corresponding to three and six moles, the first inflexion indicating the formation of ICl. The final inflexion is quite sharp in 4 *N*-H_2SO_4, but not so in smaller concentrations.

Presence of even a small concentration of bromide (0.03 *M*) affects the reduction process, leading to two inflexions. The final inflexion is still at six moles KI for a rapid titration. In a slow titration there are two inflexions :the first one at three moles KI, followed by the final one, not sharp, at about six moles. The formation of IBr is thus clearly indicated.

Gyani and Prasad (this *Journal*, 1955, **32**, 313) showed that potassium dichromate could be titrated potentiometrically with potassium iodide in hydrochloric and sulphuric acid solutions. Their investigations covered a wide range of acid concentrations. While confirming Hendrixon's results (*J. Amer. Chem. Soc.*, 1921, **43**, 1309) that accurate titrations were possible in 2*N*-H_2SO_4, they also found that provided sufficient time was allowed for equilibrium, the correct end-point corresponding to

$$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$$

could be obtained with weaker solutions. They found that the reduction of dichromate took place in two well-defined steps in HCl, corresponding to the formation of ICl (3 moles KI) and complete reduction of dichromate (6 moles KI). The reaction in HCl was quicker. It appears therefore that chloride ions may materially affect the reduction of dichromate by KI, and so also may bromide ions. We therefore undertook these potentiometric titrations in H_2SO_4 solutions, chlorides and bromides being present in varying quantities.

Experimental

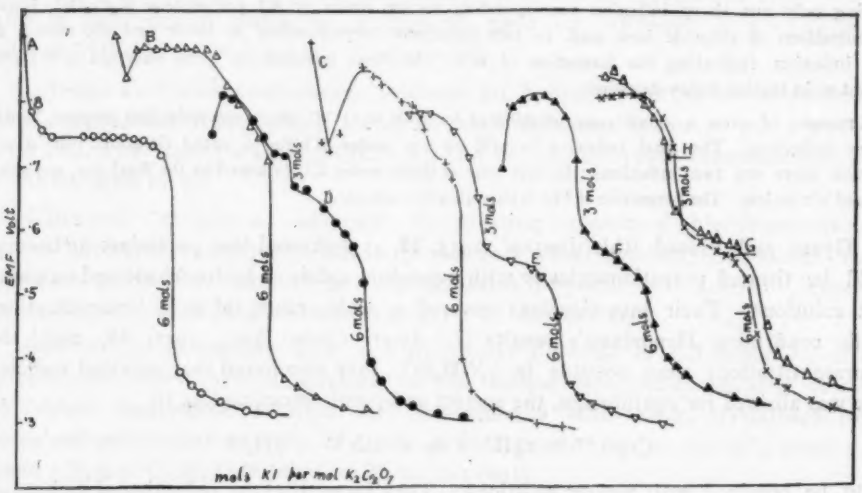
The Reaction between $K_2Cr_2O_7$ *and* KI *in presence of* Cl^-.—The experimental procedure has been described previously by Gyani and Prasad (*loc. cit.*). 0.005 *M*-Dichromate (100 c.c.) usually in 4*N*-H_2SO_4 was titrated with normal KI in the burette. Varying quantities of chloride were present as noted below.

(A) 0.03 *M*-NaCl	(C) 0.03 *M*-NH_4Cl	(E) Saturated NaCl
(B) 0,03 *M*-KCl	(D) *N*-NaCl	(F) Saturated NH_4Cl

Two more titrations were carried out in presence of saturated NaCl (G) in 2*N* acid, (H) in normal acid. The corresponding graphs are shown in Fig. 1.

In A, B and C, the mixture became red after the first c. c. of KI added, but in D, E, F and G, the red colour initially produced became pale greenish yellow on shaking till the first inflexion was reached, after which the yellow changed sharply to red. Except in F, iodine was ultimately precipitated. Initial dips were observed in the graph A, B and C, but were not reproducible. They all showed steep inflexions at 6 moles KI per mole $K_2Cr_2O_7$. The graphs D to G show two inflexions: the first at 3 moles and the second at 6 moles KI. The first one in D was only barely perceptible. The second one became less and less steep passing from E to H (smaller concentrations of H_2SO_4).

FIG. 1



Reaction in presence of Bromide Ions.—These titrations were repeated in presence of bromides: (A) 0.03*M*-KBr + 4*N*-H_2SO_4, (B) 0.03 *M*-KBr + *N*-acid, (C) *M*-KBr + 4*N* acid, (D) *M*-KBr + 2*N*-acid and (E) saturated KBr + 4*N* acid. All the reaction mixtures, except A and B, were kept in glass-stoppered bottles for 24 to 48 hours, before titration. This slight change in procedure was suggested by the quite steep (but not reproducible) initial inflexions in graphs A and B. The results are summarised in Table I; graphs appear in Fig 2.

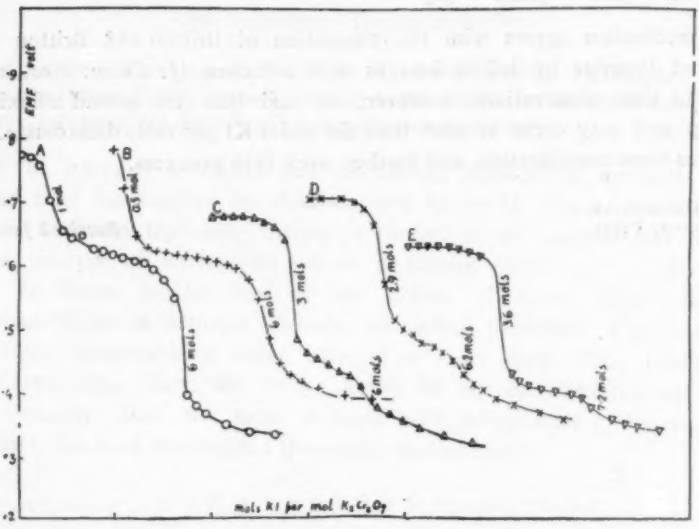
TABLE I

Graph.	Normality of KBr.	Normality of H_2SO_4	Period of storage.	Moles KI/mole $K_2Cr_2O_7$ Ist infl.	Moles KI/mole $K_2Cr_2O_7$ 2nd infl.	Remarks
A	0.03	4.0	Nil	1.0	6.0	
B	0.03	1.0	"	0.5	6.0	
C	1.00	4.0	24 hrs	3.0	6.0	2nd infl. not steep
D	1.00	2.0	"	2.9	6.2	Do
E	Sat.	4.0	48	3.6	7.2	Do

It will be seen that neither the first nor the second inflexion is independent of conditions, the first, being much less so. A decrease in the concentration of H_2SO_4

appears to bring about a decrease in the KI consumed (for the first inflexion) which is increased by increasing KBr concentration. When much bromide is present, the total KI required is more than is necessary for the complete reduction of $K_2Cr_2O_7$.

FIG. 2



The colour of the reaction mixture in A and B at the beginning of the titration had a greenish tinge, whereas in C, D and E, it was dark greenish yellow, indicating a gradual reduction of $Cr_2O_7^{2-}$ to Cr^{3+}. When the first drops of KI were added to A or B, the mixture turned deep red which changed to greenish yellow on shaking. This persisted till the first inflexion appeared when it changed to red and, iodine was precipitated. Addition of KI in C, D and E produced iodine which redissolved, developing a brown colour. This changed to deep reddish brown quite sharply at the first inflexion.

DISCUSSION

Fig. 1 shows that if enough chloride (at least normal) be present, the reduction of $K_2Cr_2O_7$ by KI takes place stepwise, ICl being formed as an intermediate compound. The reactions then are

(*i*) $Cr_2O_7^{2-} + 14H^+ + 14Cl^- + 3I^- = 2CrCl_3 + 7H_2O + 5Cl^- + 3ICl$

(*ii*) $3\,ICl + 3I^- = 3I_2 + 3\,Cl^-$.

It has been noted previously by Gyani and Prasad (*loc. cit.*) that $N/2$-HCl fails to produce the first inflexion, which agrees with the present observations.

A much smaller concentration of bromide can bring about the two-stage reduction of potassium dichromate, a concentration of even 0.03N being enough (Table I). There is nothing against the supposition that bromine is liberated in the first instance

which reacts with KI to furnish IBr_2, followed by liberation of I_2 with further addition of KI. The reactions may be written as follows:

(*iii*) $K_2Cr_2O_7 + 6KBr + 7H_2SO_4 = 4K_2SO_4 + 3Br_2 + Cr_2(SO_4)_3$,
(*iv*) $3Br_2 + 3KI = 3KBr + 3IBr$, and
(*v*) $3IBr + 3KI = 3KBr + 3I_2$.

This mechanism agrees with the suggestion of Britton and Britton concerning reduction of bromine by iodide ions in acid solutions (*J. Chem. Soc.*, 1952, 3879). Contrary to their observations, however, we find that the second inflexion is never quite steep and may occur at more than six moles KI per mole dichromate. Reaction (*iii*) deserves more consideration, and further work is in progress.

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ACTION OF NITROGEN TETROXIDE AND ITS THERMAL DISSOCIATION PRODUCTS ON BARIUM PEROXIDE

By Vasantrai Trambaklal Oza

Action of nitrogen tetroxide and its thermal dissociation products on BaO_2 has been investigated. No nitrite is formed even at 400°. The percentage conversion to nitrate increases with rise in temperature, indicating that the reduction is dependent on temperature.

Action of nitrogen tetroxide and its thermal dissociation products on sodium peroxide has been investigated by Addison and Lewis (*J. Chem. Soc.*, 1953, 1874) in which it is shown that only nitrate is formed at all temperatures below 140°, and that a mixture of nitrite and nitrate is formed above 140°. The formation of nitrite is shown to be due to the action of nitric oxide, formed as a result of dissociation of nitrogen dioxide, on sodium peroxide. PbO_2 is supposed to afford $Pb(NO_3)_2$ quantitatively when allowed to react with N_2O_4 (Dennstedt and Hasslev, *Chem. Ztg.*, 1907, **33**, 133). Action of nitrogen tetroxide or dioxide on any other peroxide does not seem to have been investigated; the action of the former on BaO_2 has been investigated thoroughly in this paper.

Experimental

BaO_2 was Merck's extra pure quality chemical and was analysed before use. Nitrogen tetroxide was prepared after Oza, Oza and Thaker (*J. Chem. Soc.*, 1955, 2457). The apparatus used for the purpose was also the same as in Oza *et al.* (*loc. cit.*).

BaO_2 was allowed to be in contact with the N_2O_4 or NO_2 for one and half hours at 0° and 30°. At other temperatures the heating bath or furnace was maintained around the reaction tube for half an hour only and immediately afterwards the temperature was brought to 30°, and all nitrous fumes were absorbed out in alkali. In none of the experiments any residual gas was removed through the Sprengel pump. Residue at the end of each experiment was carefully weighed and treated with CCl_4 to remove absorbed nitrogen tetroxide, if any, dried with ether and reweighed. In none of the experiments N_2O_4 or NO_2 was found to be absorbed. The residue was then dissolved in water and made up to a known volume through filtration in order to remove insoluble BaO_2. A known volume of the solution was taken and CO_2 was passed through the solution in order to precipitate barium as $BaCO_3$. The resulting H_2O_2 was destroyed by boiling. Blank experiments were done with mixtures of $Ba(NO_2)_2$ and H_2O_2 in solution to test the stability of the nitrite in presence of peroxide, and it was found that $Ba(NO_2)_2$ was completely stable in a boiling dilute solution of H_2O_2. The solution was then analysed for nitrate after having ascertained that no nitrite was formed in any experiment. The alkali solution was analysed both for nitrite and nitrate, and within experimental error only N_2O_4 or NO_2 was found to be the product in the gaseous mixture. The results are shown in Table. I

TABLE I

1	2	3	4	5	6	7		8	9
						Residue		N_2O_4 left.	G. mols of NO_2 consumed.
Expt. No.	Temp.	Period of contact.	BaO_2 taken.	N_2O_4 taken.	Residue formed.	$Ba(NO_3)_2$ formed.	BaO_2 left (calc.).		
1	0°	1½ hrs.	0.110 g.	0.3730 g.	0.1101 g.	...	0.1101 g.	0.3729 g.	...
2	30°	1½	0.100	0.1700	0.1000	...	0.1000	0.1700	...
3	140°	½	0.109	0.2546	0.1090	...	0.1090	0.2547	...
4	170°	½	0.124	0.3010	0.1256	0.00448 g. (0.170×10^{-4})	0.1211	0.2994	(0.356×10^{-4})
5	200°	½	0.100	0.3252	0.1031	0.00894 (0.357×10^{-4})	0.0942	0.32175	(0.706×10^{-4})
6	250°	½	0.110	0.2692	0.1167	0.01341 (0.512×10^{-4})	0.1013	0.2643	(1.046×10^{-4})
7	300°	½	0.100	0.1710	0.1170	0.01782 (0.680×10^{-4})	0.09854	0.16474	(1.360×10^{-4})
8	350°	½	0.105	0.2000	0.1139	0.03117 (1.19×10^{-4})	0.0827	0.189	(2.390×10^{-4})
9	400°	½	0.103	0.1960	0.1271	0.0402 (1.530×10^{-4})	0.0769	0.1816	(3.130×10^{-4})

Gram-molar quantities are shown in parenthesis.

DISCUSSION

No nitrite is formed under the experimental condition even at 400°. The percentage conversion to nitrate increases with the rise in temperature, indicating that the reaction is largely temperature dependent. From the table it can be seen that for every gram molecular quantity of BaO_2 used up, 2 gram molecular quantity of NO_2 is utilised to form one gram molecular quantity of $Ba(NO_3)_2$, which clearly indicates that the reaction in gaseous system runs according to the following equation.

$$BaO_2 + 2NO_2 \longrightarrow Ba(NO_3)_2$$

nitrite forming reaction, *i.e.*

$$BaO_2 + 2NO \longrightarrow Ba(NO_2)_2$$

is found to be quite absent under the experimental condition. This is perhaps due the property of BaO_2

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A NEW METHOD OF PREPARATION OF ANHYDROUS ACETATES OF RARE-EARTH ELEMENTS

By S. Panda and D. Patnaik

The anhydrous acetates of thorium, cerium and lanthanum have been prepared by the action of the respective nitrate on acetic anhydride. This method can be applied, in general, for preparation of the acetates of other rare earths and elements, the nitrates of which are partially soluble in acetic anhydride.

Preparation of anhydrous salts, particularly acetates of rare-earth elements, is not available in literature. In our investigation to effect the separation of the rare-earths, the salts of thorium, cerium(ous) and lanthanum were prepared by a method other than the usual one of dissolving the oxides, hydroxides or carbonates in acetic acid. By our method anhydrous salts are obtained, while the known methods furnish hydrated salts. The anhydrous salts of other elements, nitrates of which are partially soluble in acetic anhydride, can also be prepared by this method.

Experimental

Cerium nitrate and acetic anhydride used were E. Merck chemicals. Thorium nitrate was of B. D. H. Analar quality. Lanthanum nitrate was prepared in the laboratory.

Acetic anhydride (10 c.c. in each case) was treated with the hydrated nitrates (3 g. each). The mixtures were heated over a sand-bath till the nitrous fumes had ceased to evolve. In case of thorium, the anhydrous acetate came down as a white granular powder. On heating the mixture containing cerium, at first a slightly yellow-coloured resinous mass separated which was found to contain nitrogen. On further heating and mechanically breaking up the resinous mass, a slightly yellowish precipitate settled down in granular form from the yellow solution. The yellow colour of the solution and the precipitate was mainly due to a portion of the cerium salt being in the ceric state (Patnaik and Panda, *Curr. Sci.*, 1956, **25**, 287). A few drops of water were used to reduce the ceric salt which was produced in the mixture. The anhydrous cerous acetate was thus obtained as a white crystalline powder. The lanthanum salt was obtained in the same way as the cerium salt. The white precipitate, in each case, was filtered, washed with acetic anhydride and kept in a vacuum desiccator over solid NaOH to free them of solvents. The compounds on being tested were found free of nitrogen.

The oxide contents of the salts were obtained by ignition of weighed quantities of the salts in tared platinum crucibles over a Teclu burner. The results are recorded in Table I along with the calculated values. The acetate contents of the salts were determined by acidimetric titration with phenolphthalein as indicator. Weighed amount of the salt was dissolved in water in well-covered beakers and hydrolysed by boiling with

a standard NaOH solution (1.007 $N/10$, 30 c.c.). The precipitate was separated quantitatively by filtration. The filtrate was titrated with standard sulphuric acid to ascertain the volume of standard alkali consumed by acetic acid, liberated by hydrolysis. The alkali values are recorded in Table I along with that of the calculated values.

TABLE I

Expected compound.	Salt taken.	Weight of oxide. Calc.	Found.	Salt taken	Volume of alkali. Calc.	Found.
$Th(C_2H_3O_2)_4$	0.2890 g.	0.1631 g.	0.1614 g.	0.2150 g	18.25 c c	18.30 c.c.
	0.2268	0.1280	0.1277	0.1580	16.82	16.85
$Ce(C_2H_3O_2)_3$	0.2283	0.1239	0.1221	0.1806	16.96	17.15
	0.1672	0.0907	0.0893	0.2006	18.85	19.00
$La(C_2H_3O_2)_3$	0.2940	0.1516	0.1460	0.1662	15.68	15.70
	0.2558	0.1320	0.1268	0.1668	15.73	15.90

The rare-earth nitrate in the reaction with acetic anhydride is converted finally into acetate, which being sparingly soluble in the solvent separates out as fine crystalline precipitates. Calculations indicate that hydrated or basic acetates are not formed in our experiments. Thus, the anhydrous acetates of the rare-earth elements have been prepared, as shown by the data recorded above.

It has been observed that the reaction proceeds in stages which cause the separation of intermediate resinous compounds during the preparation of lanthanum and cerium acetates. The elimination or deionisation of nitrate ion in acetic anhydride shows all the characteristics of a chain reaction. Further application of this reaction in the field of rare-earth chemistry is in progress and will be reported in future.

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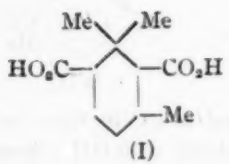
SESQUITERPENES AND RELATED SUBSTANCES. PART IV. SYNTHESIS OF A STRUCTURAL ISOMER OF THE DICARBOXYLIC ACID, $C_{11}H_{18}O_4$*, A DEGRADATION PRODUCT OF CEDRENE

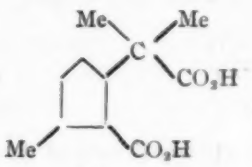
By Phanindra Chandra Dutta **

1:3:3-Trimethyl*cyclo*hexane-2:4-dicarboxylic acid was synthesised with a view to comparing its properties with a C_{11}-dicarboxylic acid, a degradation product of cedrene, and these were found to be different.

Through a series of oxidative degradations on cedrene, a dicarboxylic acid, $C_{11}H_{18}O_4$, was isolated (Plattner *et al.*, *Helv. Chim. Acta*, 1943, **26**, 1553). As a result of further degradative work on this acid, its constitution was suggested to be one of the following (Plattner *et al.*, *Chimia*, 1948, **2**, 248; *Helv. Chim. Acta*, 1953, **36**, 1845).



(I)



(II)

More recently, the structure of cedrene has been completely elucidated from degradative and synthetic standpoints (Plattner *et al.*, *loc. cit.*; Stork *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 3291; 1955, **77**, 1073) and the structure (II) of the C_{11}-acid has been fully established.

Experiments described herein were carried out in 1948-49 and dealt with the synthesis of the acid represented by structure (I). The properties of this synthetic acid were, however, found to be quite different from that isolated from the natural source.

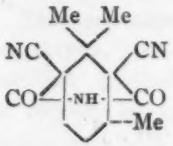
αα-Dicyano-ββ-dimethylglutarimide was condensed with 1:3-dibromobutane (Perkin, *J. Chem. Soc.*, 1914, **105**, 1356) in alcoholic solution. The condensation can proceed evidently in different ways and the final condensation product is found to depend considerably on the duration of refluxing of the reaction mixture. If the refluxing period is limited to about 8 hours, a considerable quantity of a crystalline material separates out from the reaction mixture on dilution with acidulated water, from which the desired condensation product (III) can be isolated in about 5% yield by repeated crystallisations. The crystalline material recovered from the mother-liquor probably contains, in addition to (III), an unsaturated compound, most probably (IVa) and/or a bromo compound (IVb) which have been formed through the normal condensation of the primary bromine and

* This investigation was carried out in 1948-49 during the tenure of a foreign travelling Fellowship awarded by the University of Calcutta in 1947 and constituted a part of the report submitted to the University.

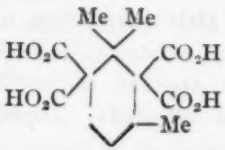
** Cf. Plattner *et al.*, *Helv. Chim. Acta.*, 1953, **36**, 1849. foot note 2.

with or without the elimination of the secondary bromine. This view has been arrived at mainly from a study of the hydrolysis results. If the period of refluxing be extended to 24 hours, the yield of the crystalline material decreases considerably. Attempts at acidic hydrolysis of the imide (III) being not very promising, it was hydrolysed by refluxing with alkali. The tetracarboxylic acid (V) was decarboxylated in the usual way and the oily acid, so obtained, was isolated as its anhydride (VI). The properties of the synthetic anhydride and also I.R. studies show considerable divergence from the anhydride of the C_{11}-acid.

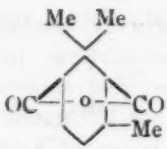
To characterise the synthetic product further, it was hydrolysed to the acid (I) which was an oil at room temperature, but solidified to small needle-shaped crystals, when cooled in ice. This was converted into *p*-bromophenacyl derivative, which separated from the reaction mixture in about 60% yield in a quite pure form, and from which only one form of crystals was isolated. It appears that the anhydride is quite homogeneous in nature.



(III)

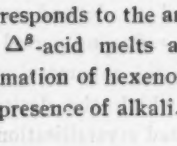


(V)

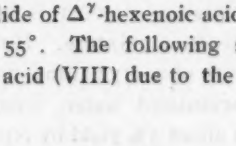


(VI)

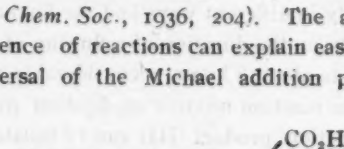
The nature and constitution of the products (IVa) and/or (IVb) have been arrived at in an indirect way. Because of the very close similarity with (III), these could not be prepared in a very pure state. On alkaline hydrolysis, the impure product afforded a mixture of crystalline acids, which on thermal degradation was treated with acetic anhydride. On distillation, a low-boiling acidic fraction has been isolated along with a higher boiling product which has been identified as the anhydride (VI). The lower-boiling fraction was warmed with alkali to remove any acetic anhydride and was finally purified by distillation. The analytical values correspond to that of an unsaturated hexoic acid. It takes up one molecule of hydrogen catalytically. The saturated acid has been characterised by its anilide and other physical properties and is found to be identical with hexoic acid. The unsaturated acid is found to develop a strong yellow coloration with tetranitromethane; it furnishes an anilide melting at 85° and which corresponds to the anilide of Δ^{γ}-hexenoic acid (*J. Chem. Soc.*, 1936, 204). The anilide of Δ^{β}-acid melts at 55°. The following sequence of reactions can explain easily the formation of hexenoic acid (VIII) due to the reversal of the Michael addition process in presence of alkali.



(IVb)



(IVa)



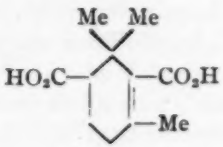
(VIII)

Since $\beta\beta$-dimethylacrylic acid decomposes into butylene and carbon dioxide at about 205°, it is quite natural that during decarboxylation at 200°-210°, this component is lost, and from the lower-boiling portion only hexenoic acid is isolated.

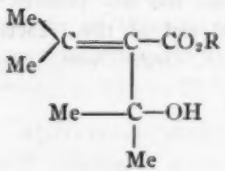
Based on the quantity of the formation of the anhydride (VI) and hexenoic acid (VIII), it is found that in the initial condensation of the dibromide, (III) is formed to the extent of about 15 to 20%, and other products constitute the major fraction to the extent of about 40% of the theory.

Some preliminary experiments were carried out to utilise the Diels-Alder reaction between ethyl sorbate and substituted ethyl acrylates to synthesise tetrahydro*iso*phthalic acids, but in this case ethyl $\beta\beta$-dimethylacrylate failed to act as a dienophile.

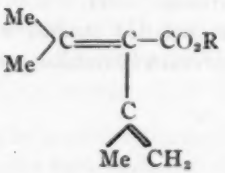
Since the C_{11}-acid contains three asymmetric centres, the synthetic and natural acids may be diastereoisomers because the asymmetric centre involving the methyl group has not been clearly defined in both the acids. Consequently, the next attempt was directed to the synthesis, according to the following scheme, of the C_{11}-dehydro acid. The constitution of the dehydro-acid has been suggested as (IX) from its mode of formation from the natural C_{11}-acid (Plattner *et al.*, *Helv. Chim. Acta*, 1943, **26**, 1553).



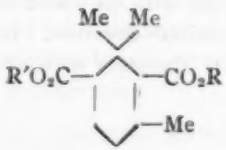
(IX)



[X: R=Et; XI: R=H]



[XII: R=H; XIII: R=Me]



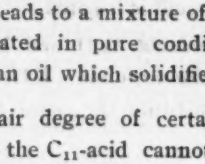
[XIV: R=Me; R′=Et; XV: R=R′=H].

With this end in view, methylmagnesium iodide was allowed to react with ethyl *iso*-propylidene-acetoacetate at a low temperature. Two fractions were isolated, the higher boiling one consisted of the hydroxy-ester (X) and the corresponding doubly unsaturated ester. From the lower-boiling fraction, the doubly unsaturated acid (XII) could be isolated on hydrolysis with alkali. On hydrolysis of the main reaction product, an oil was obtained containing varying proportions of (XI) and (XII), from which, however, (XII) was isolated. In one case, crystals of (XII) were obtained from the reaction mixture. The crude acid was dehydrated with *p*-tolylsulphonyl chloride at 130°-135° and the doubly unsaturated acid was isolated as its methyl ester (XIII) on esterification with diazomethane. This ester on hydrolysis with alkali gave back the acid (XII) and took up two molecules of hydrogen on catalytic hydrogenation. The ester (XIII) was condensed with ethyl acrylate according to the Diels-Alder reaction at 230°-240° in presence of a trace of hydroquinone to furnish (XIV) in about 30% yield. The unsaturated

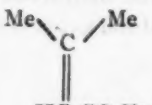
acid (XV), obtained on hydrolysis, melts at 214-15°. It shows considerable depression in m.p. when mixed with the unsaturated acid isolated from cedrene. On catalytic reduction, it leads to a mixture of saturated acids from which no particular component could be isolated in pure condition. The mixture of saturated acids afforded an anhydride as an oil which solidified in the cold.

With a fair degree of certainty these experimental results may be explained on the basis that the C_{11}-acid cannot be represented by the *cyclo*hexane derivative (I). Consequently it becomes of interest to synthesise the corresponding *cyclo*pentane derivative (II), which is considered the only other alternative structure of C_{11}-acid; some preliminary experiments in this direction are recorded here.

The most obvious method appeared to be the condensation of the two following components according to Michael, but the condensation failed to proceed to any appreciable extent (cf. Bhattacharyya, this *Journal*, 1945, **22**, 214).



and



Another attractive scheme appeared to be the condensation of ethyl α-bromo*iso*butyrate with the above *cyclo*pentanone ester. The condensation did not proceed in the desired direction. Later on, detailed studies were carried out of this reaction in this laboratory with interesting results (Talukdar and Bagchi, *J. Org. Chem.*, 1955, **20**, 25).

Experimental

2 : 2 : 4-*Trimethyl*-1 : 3-*dicyanohexahydroisophthalimide* (III).—Sodium (7.3 g.) was dissolved in absolute alcohol (96 c.c.) and to the cooled solution was added αα'-dicyano-ββ-dimethylglutarimide (19 g., Vogel, *J. Chem. Soc.*, 1934, 1760) and refluxed for ½ hour. Refluxing was continued for about 8 hours after adding 1 : 3-dibromobutane (22 g.) and then it was poured into water (600 c.c.) containing HNO_3 (20 c.c.). An oil separated which gradually solidified; on standing in the cold, the solution became full of crystals. It was filtered and it weighed 16 g. It was crystallised repeatedly from methanol and acetic acid till the m. p. became constant at 160-61°; yield 1.2 g. (Found: C 63.59; H, 6.09; N, 17.26. $C_{12}H_{15}O_2N_3$ requires C, 63.66; H, 6.16; N, 17.20 per cent).

2 : 2 : 6-*Trimethylcyclohexyl*-1 : 1 : 3 : 3-*tetracarboxylic Acid* (V).—The above imide (1 g.) was hydrolysed by refluxing for 48 hours with NaOH (2.5 g.) in water (20 c.c.). The solution was acidified and extracted repeatedly with ethyl acetate. On removal of the solvent, an oil remained which solidified in needles, m.p. 90°-102°, yield 1 g. It was

free from nitrogen. It was repeatedly crystallised from a mixture of acetone and benzene, when the m.p. rose to 119-22° with previous softening at about 100°. (Found: C, 51.95 ; H, 6.52. $C_{12}H_{18}O_8$ requires C, 51.6 ; H, 5.9 per cent).

Anhydride of 2 : 2 : 6-*trimethylcyclohexyl*-1 : 3-*dicarboxylic Acid* (VI).—The above crude tetracarboxylic acid (1 g.) was decarboxylated at 200°-210° for 15 minutes. The residue was then refluxed with acetic anhydride (2 c.c.) for 2 hours and distilled in vacuum. The anhydride passed over at 91-93°/0.2 mm., yield 260 mg. (Found : C, 67.17 ; H, 8.39. $C_{11}H_{16}O_3$ requires C, 67.32 ; H, 8.22 per cent).

2 : 2 : 6-*Trimethylcyclohexyl*-1 : 3-*dicarboxylic Acid* (I).—The above anhydride (100 mg.) was heated with 2*N*-NaOH solution (2 c.c.) on the water-bath for 10 minutes. On acidification the acid separated as an oil, which solidified to needle-shaped crystals on cooling in a freezing mixture. The acid (300 mg.) yielded the p-*bromophenacyl* derivative (470 mg., m.p. 70°), which on recrystallisation from alcohol melted at 74-75°. The sample was dried at 50° in high vacuum for 24 hours for analysis. (Found : C, 53.6 ; H, 4.9 ; Br, 26.6. $C_{27}H_{28}O_6Br_2$ requires C, 53.3 ; H, 4.64 ; Br, 26.3 per cent).

The combined mother-liquor, after separation of (III) through crystallisation, was diluted with water and the crystals were collected. This product (4 g.) was hydrolysed with NaOH (6 g.) in water (55 c.c.) by refluxing for 40 hours. It was repeatedly extracted with ethyl acetate after acidification ; the solid residue left on removal of the solvent was decarboxylated at 200°-210°, and next treated with acetic anhydride in the usual way. On distillation, a fraction (0.85 g.) was obtained boiling at 50°-60°/0.1 mm. and another fraction (0.3 g.) boiling at 90-95°/0.1 mm. The second fraction was found to be identical with the anhydride (VI), as shown by the following analysis and by conversion into the low-melting needle-shaped crystals of the dicarboxylic acid (I). (Found : C, 67.32 ; H, 8.36. $C_{11}H_{16}O_3$ requires C, 67.32 ; H, 8.22 per cent).

Δ^{γ}-*Hexenoic Acid* (VIII).—The lower-boiling fraction (1 g.) was heated with 10% NaOH solution (5 c.c.) on the water-bath and the clear solution was acidified and extracted with ether. On distillation a clear oil (0.6 g.) passed over at 60°/0.1 mm. It developed a yellow colour with tetranitromethane. This acid (1.2 g.) took hydrogen (245 c.c.) in 20 minutes in acetic acid solution in presence of platinum oxide catalyst (calc. for one double bond, 240 c.c.). The anilide was prepared in the usual way from the unsaturated acid, which on crystallisation from ethyl acetate and petroleum ether (after decolorisation with charcoal) melted at 84-86° (lit. m.p. 87°). No isomeric anilide could be detected in the mother-liquor. (Found : C, 76.13 ; H, 9.95. $C_{12}H_{15}ON$ requires C, 76.15 ; H, 9.99 per cent).

Hexoic Acid.—The reduced acid, obtained above distilled at 60°/0.15 mm. It solidified when cooled in a freezing mixture (lit. -1.5°). The anilide, prepared in the usual way, crystallised from dilute methanol and melted at 92°, alone or with an authentic specimen. (Found : C, 75.38 ; H, 8.92. $C_{13}H_{17}ON$ requires C, 75.35; H, 8.96 per cent).

Ethyl 2-*isopropyliden*-3-*hydroxyisovalerate* (X).—Ethyl *iso*pro ylidene-acetoacetate (46 g., 114-15°/21 mm. or 104-105°/15 mm.), dissolved in petroleum ether (200 c.c.),

was treated with stirring at -6° to -12° with a Grignard's solution prepared from magnesium (7.5 g.) and methyl iodide (50 g.). At first there was a vigorous reaction. After the addition was complete, it was stirred for another hour till the temperature rose to zero degree. The dark oily liquid together with the yellow solid complex was decomposed with a saturated solution of ammonium chloride and extracted with ether. The ethereal solution was dried and distilled. The first fraction was collected up to 108°/16 mm. (14 g.) and the second fraction (28 g.) boiling at 112-18°/16 mm. was again distilled, when it passed over at 113-16°/16 mm. as a light yellow mobile oil, yield 22 g. (Found: C, 66.31 ; H, 9.25. $C_{10}H_{16}O_3$ requires C, 64.49 ; H, 9.74 per cent. $C_{10}H_{16}O_2$ requires C, 71.39 ; H, 9.19 per cent).

α-iso*Propyliden-β-hydroxy*isov*aleric Acid* (XI).—The above ester (5 g.) was refluxed for 2 hours with 10%KOH solution (50 c.c.). The unchanged oil was removed with ether and the alkaline solution was acidified and extracted with ether overnight. On removal of the solvent, an oil (3 g.) remained which partly solidified. The crystals were collected (0.6 g.) and washed with ether. On two crystallisations from ethyl acetate, it melted at 132-33° with evolution of a gas. (Found: C, 60.55 ; H, 8.31. $C_8H_{14}O_3$ requires C, 60.74 ; H, 8.91 per cent).

On hydrogenation in acetic acid solution in presence of platinum oxide catalyst, the compound took 1.1 moles of hydrogen.

α-iso*Propyliden-β-methylvinylacetic Acid* (XII).—The crude oil (3 g.), obtained from the above hydrolysis, was heated for 15 minutes at 130°-140° with *p*-tolylsulphonyl chloride (30 mg.). On cooling, water was added when the crystals melting at 45-48° separated out. This was twice crystallised from methanol containing a little water. It was obtained in stout plates, m.p. 51-52°, yield 2 g. (Found: C, 68.48 ; H, 8.65. $C_8H_{12}O_2$ requires C, 68.54 ; H, 8.63 per cent). 0.22 g. of the substance took hydrogen (76 c.c.) corresponding to two double bonds (calc., 70 c.c.).

Methyl α-iso*Propyliden-β-methylvinylacetate* (XIII).—The crude oily product (3 g.), obtained above on heating with *p*-tolylsulphonyl chloride, was taken up in ether and esterified with an ethereal solution of diazomethane until a slight yellow colour persisted. On distillation, the desired ester (2 g.) was obtained as a clear colorless oil of b.p. 60-62°/11 mm. together with a higher-boiling fraction (0.3 g.), b.p. 108-10°/18 mm. (Found: C, 69.98 ; H, 9.02. $C_9H_{14}O_2$ requires C, 70.10 ; H, 9.15 per cent).

Methylethyl 1 : 3 : 3-*Trimethyl*-Δ^1-cyclo*hexenyl*-2 : 4-*dicarboxylate* (XIV).—The above diene ester (3 g.) and ethyl acrylate (2.5 g.) and a pinch of hydroquinone were heated in a sealed tube at 230°-240° for 40 hours, in a bomb tube, half-filled with water. The mass became brown and was distilled, when a little of the diene ester (1 g.) was recovered together with the desired product (1.7 g) boiling at 100°-120°/0.1 mm., and a resin remained in the flask. The higher-boiling fraction was redistilled when it passed over at 103-105°/0.2 mm., yield 1.5 g. (Found: C, 66.18; H, 8.56. $C_{14}H_{22}O_4$ requires C, 66.11 ; H, 8.72 per cent).

1 : 3 : 3-*Trimethyl*-Δ^1-cyclo*hexenyl*-2 : 4-*dicarboxylic Acid* (XV).—KOH (0.6 g.) was dissolved in methanol (3 c.c.) and to this was added the above ester (0.4 g.) and

refluxed for 24 hours under nitrogen atmosphere. It was diluted with water, the alcohol removed on the water-bath, and acidified, when a gum separated which gradually crystallised out. It was twice crystallised from ethyl acetate, m.p. 214-15°. When mixed with the unsaturated acid from cedrene, it melted at 167-73°. (Found: C, 61.88; H, 7.86. $C_{11}H_{16}O_4$ requires C, 62.25; H, 7.60 per cent).

These experiments were carried out in the chemical laboratories of E.T.H., Zürich, Switzerland and the author places on record his grateful thanks to Prof. Plattner and to Dr. A. Fürst for their kind help and encouragement and also for the laboratory facilities. Thanks are also due to the University of Calcutta for the award of the Ghosh Travelling Fellowship in science.

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SESQUITERPENES AND RELATED SUBSTANCES. PART V. SYNTHESIS OF ISOMERIC METHYL*iso*PROPYL*cyclo*HEPTANONES*

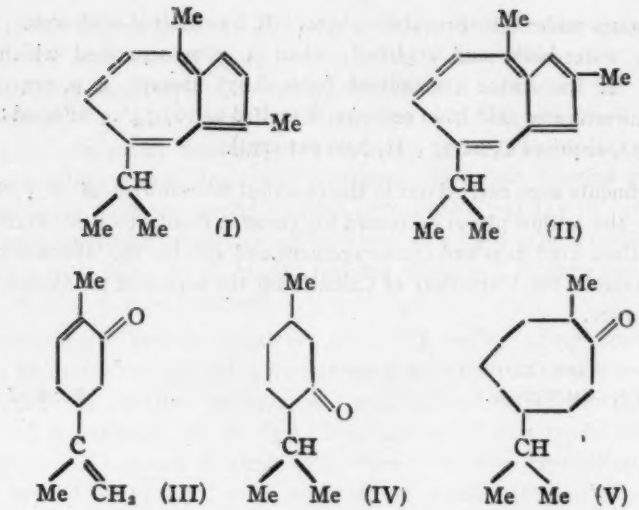
BY PHANINDRA CHANDRA DUTTA

Synthesis of 2-methyl-5-*iso*propyl- and 2-*iso*propyl-5-methyl*cyclo*heptanones has been described. These ketones are expected to be of use in the synthesis of substituted azulenes.

For the synthesis of substituted azulenes, S-guaiazulene (I) and Se-guaiazulene (II), isolated from naturally occurring sesquiterpenes, the alkylated *cyclo*heptanones constitute important intermediates. The distribution of alkyl residues in (I) and (II) has finally been confirmed by synthesis (Plattner *et al.*, *Helv. Chim. Acta*, 1949, **32**, 2137; Pliva *et al.*, *Coll. Czech. Chem. Com.*, 1951, **16**, 158).

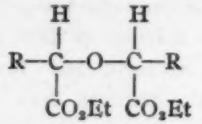
In the structural framework of carvone (III) and menthone (IV), the methyl and *iso*propyl groups are properly distributed and these may serve as convenient starting materials to realise the synthesis of these important azulenes. By applying the usual ring-expansion methods to these ketones, seven-membered ring ketones have been synthesised, but the constitution of these ketones could not be definitely settled in view of the alternative structures, possible from theoretical considerations (cf. H.C. Neumann, Dissertation, E.T.H., Zürich, 1949). It has been thought desirable to devise other methods for the synthesis of the seven-membered ketones from carvone and menthone, which will leave no ambiguity so far as the constitution of the final products is concerned.

* This investigation was carried out in 1948-49 during the tenure of a Foreign Travelling Fellowship awarded by the University of Calcutta in 1947 and constituted a part of the report submitted to the University.

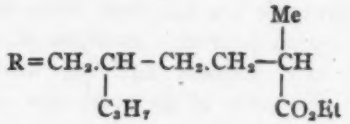


Experiments initiated with a view to synthesising the ketone (V) were carried out with the keto-ester (VI : Simonsen *et al.*, *J. Chem. Soc.*, 1935, 316), which constituted the major product in the condensation of ethyl oxalate and tetrahydrocarvone. This product can be isolated in a reproducible yield, but the yield of the keto-ester (VI) appears to depend considerably on the presence of the quantity of sodium ethoxide. If ethyl oxalate is used in excess to keep the concentration of free sodium ethoxide as low as possible, the yield of the keto-ester falls considerably and during alkaline hydrolysis, a considerable quantity of tetrahydrocarvone is recovered. Reduction of the keto-group in (VI) was attempted by refluxing for a prolonged period with amalgamated zinc in alcoholic solution, saturated with dry hydrogen chloride (Smith and Rouault, *J. Amer. Chem. Soc.*, 1943, **65**, 746) and the keto-ester was recovered unchanged. Similar failure was also met with in the Clemmensen reduction. Finally the keto-ester was reduced catalytically in acetic acid solution in presence of platinum oxide catalyst to furnish (VII). Replacement of the hydroxyl group with thionyl chloride and pyridine led to incomplete reaction. Next it was allowed to react with PCl_5 ; the chloro-ester (VIII) was isolated in a satisfactory yield and an undistillable residue remained in the flask. The chloro-ester (VIII) on boiling with zinc dust in acetic acid solution led to the formation of the expected ester (IX). This on hydrolysis afforded the free acid (X) in an excellent yield. The dicarboxylic acid was converted into thorium salt, which on dry distillation furnished the ketone (V) in a good yield. The ketone afforded a mixture of semicarbazones from which two fractions crystallised out. The melting points of the semicarbazones do not indicate their stereochemical homogeneity, although the ketones generated from these two types of semicarbazones have the same boiling point and refractive index but slightly different values of optical rotation. It is most likely due to the fact that the asymmetric centre carrying the methyl group undergoes partial racemisation during ketonisation as it is α-to the carbonyl group.

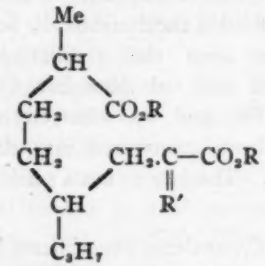
Regarding the nature of the undistillable viscous residue left in the flask after distillation of the chloro-ester (VIII), the following product (XI) appeared to constitute the major fraction quite in analogy with the action of PCl_5 on cyanohydrins (Downer and Hornung, *J. Chem. Soc.*, 1941, 505).



(XI)



In support of the ether-linkage, it was found that on prolonged boiling with hydroiodic acid and red phosphorous it led to the same acid (X) in a very good yield. This was characterised by a *p*-bromophenacyl derivative having a different melting point. The dicarboxylic acid obtained in this manner furnished the same ketone (V) on thorium salt distillation and from which again the same mixture of semicarbazones was obtained.



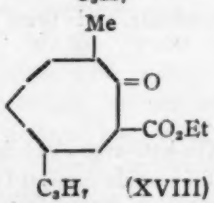
VI: R′ = O; R = Et

VII: R′ = ; R = Et

VIII: R′ = ; R = Et

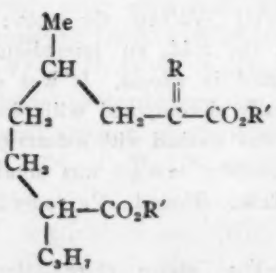
IX: R′ = H_2; R = Et

X: R′ = H_2; R = H.



(XVIII)

Synthetic investigations have also been extended in an identical way to menthone, as indicated below, to realise the synthesis of (XVII).



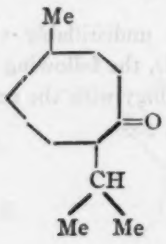
XII: R = O; R′ = Et

XIII: R = ; R′ = Et

XIV: R = ; R′ = Et

XV: R = ; R′ = Et

XVI: R = ; R′ = H



(XVII)

The fission of the condensation product from menthone and ethyl oxalate in presence of two molecules of sodium ethoxide proceeds only with a comparatively poor yield. Some of the experimental conditions have been tried, but the optimum conditions still remain to be found out. The keto-ester (XII) was reduced to the hydroxy-ester (XIII) catalytically and the latter was again converted into the chloro-ester (XIV) along with a non-distillable residue. It was reduced in acetic acid solution with zinc dust to furnish (XV), which on hydrolysis afforded the dicarboxylic acid (XVI) in a very good yield. The non-distillable residue from the distillation of the chloro-ester (XIV) was refluxed with hydriodic acid and red phosphorus, resulting in the formation of the dicarboxylic acid (XVI). The acid was characterised by a well-defined *p*-bromophenacyl derivative. The acid was converted into the ketone (XVII) through dry distillation of the thorium salt. The ketone has a smell, strongly reminiscent of menthone.

With a view to realising the synthesis of a C_{15}-azulene, experiments have been successfully carried out with 2-methyl-5-*iso*propyl*cyclo*heptanone, and these results will be published in a future communication.

Experimental

Ethyl 1-Hydroxy-6-methyl-3-isopropylsuberate (VII).—The keto-ester (VI: 800 mg.) was hydrogenated in acetic acid (5 c.c.) in presence of platinum oxide catalyst (30 mg.) and absorption of the calculated amount of hydrogen was complete in half-an-hour. On filtering off the catalyst, it was distilled as a colorless oil, b. p. 135°/0.1 mm. It showed no ferric chloride coloration. (Found: C, 63.76; H, 9.99. $C_{16}H_{30}O_5$ requires C, 63.6 ; H, 9.9 per cent).

Ethyl 1-Methyl-6-chloro-3-isopropylsuberate (VIII).—When the above hydroxy-ester (3 g.) was treated with PCl_5 (2.2 g.) in the cold, an immediate reaction started and a little of the pentachloride remained in excess. It was allowed to stand at room temperature for 2 hours and finally decomposed with ice. It was extracted with ether and the ethereal solution was washed with sodium bicarbonate solution, and finally it was distilled, when the chloro-ester (2.6 g.) was obtained, b. p. 126-30°/0.1 mm. There was a residue in the flask. (Found: C, 59.85 ; H, 9.15. $C_{16}H_{29}O_4Cl$ requires C, 59.89 ; H, 9.11 per cent).

Ethyl 1-Methyl-4-isopropylsuberate (IX).—The above chloro-ester (5.5 g.) was refluxed for 12 hours with zinc dust (4 g.) in acetic acid (40 c.c.). The

solution was poured into water, extracted with ether and the ethereal solution was washed with sodium carbonate solution and finally distilled. It passed over at 115-16°/0.08 mm., yield 4 g. (Found: C, 67.09; H, 10.55. $C_{16}H_{28}O_4$ requires C, 67.09; H, 10.56 per cent).

1-Methyl-4-isopropylsuberic Acid (X).—The above ester (38 g.) was hydrolysed by refluxing with a solution of KOH (38 g.) in methanol (200 c.c.) for 20 hours. The methanol was removed on the water-bath and the solution was diluted with water, and acidified. The viscous mass was taken up in ether and finally distilled, when it passed over at 178°/0.1 mm., yield 30 g. (Found: C, 62.55; H, 9.57. $C_{12}H_{22}O_4$ requires C, 62.58; H, 9.63 per cent). The *p*-bromophenacyl derivative was prepared in the usual manner and after repeated crystallisation from alcohol melted at 77-79°; $[\alpha]_D^{16}$, + 14°.4 (c=15.3 mg/c.c. in chloroform). (Found: C, 53.67; H, 5.16. $C_{28}H_{32}O_6Br_2$ requires C, 53.86; H, 5.17 per cent).

2-Methyl-5-isopropylcycloheptanone (V).—The dicarboxylic acid (10 g.) was dissolved in alcohol (25 c.c.) and neutralised with a 10% NaOH solution, and heated to 70°. Thorium nitrate (14 g.) was dissolved in water (100 c.c.) and heated to 80°. This was vigorously stirred and to this was added the hot solution of the sodium salt all at once. It was stirred for 15 minutes more and was filtered. The precipitate was washed thoroughly with hot water to remove completely any thorium nitrate adhering to the precipitate. Next it was dried in steam, powdered and taken in a flask for dry distillation. At first it was heated to 200° to remove last traces of moisture, and towards the end water-suction was applied. The temperature was gradually raised to 350° in 2 hours. Decomposition started at 275° and finally the temperature was raised to 400° in the course of 1 hour. The distillate (5.5 g.) was taken up in ether and washed with sodium carbonate solution. On distillation in vacuum, the fraction boiling at 105-108°/12 mm. was collected. This was treated with sodium acetate and semicarbazide hydrochloride in methanol, whereupon crystals separated, which on washing with petroleum ether melted at 130-35°. This on twice crystallisation from methanol melted at 136-38°. (Found: C, 63.99; H, 10.26; N, 18.84. $C_{12}H_{23}ON_3$ requires C, 63.96; H, 10.29; N, 18.65 per cent).

The semicarbazone was mixed with an equal quantity of oxalic acid in water and steam-distilled; the ketone was obtained as a pleasant smelling liquid. It was extracted with ether and distilled, when it passed over at 105-106°/10 mm., yield quantitative; $[\alpha]_D^{16}$, + 38°.8 (c=15 mg./c.c. in alcohol); d^{16}, 0.9268; n_D^{16}, 1.4660. (Found: C, 77.94; H, 12.07. $C_{11}H_{20}O$ requires C, 78.51; H, 11.98 per cent).

The above semicarbazone on repeated crystallisations from methyl alcohol yielded a small amount of the semicarbazone of m. p. 149-51°. (Found: C, 63.95; H, 10.24; N, 18.61. $C_{12}H_{23}ON_3$ requires C, 63.96; H, 10.29; N, 18.65 per cent).

The ketone was regenerated from the semicarbazone in the usual way and distilled at 105-106°/10 mm. $[\alpha]_D^{16}$, +41° (c=15 mg./c.c. in alcohol); d^{16}, 0.9270. n_D^{16}, 1.4658. (Found: C, 78.22; H, 11.88. $C_{11}H_{20}O$ requires C, 78.51; H, 11.98 per cent).

The non-distillable residue (10 g.) from PCl_5 treatment of the hydroxy ester, described before, was refluxed for 24 hours with HI (*d* 1.7; 50 g.) and red phosphorus (10 g.). In the beginning there was too much frothing and the condenser had to be removed sometimes to distill away EtI formed in the reaction. The mixture was diluted with water and extracted with ether. From the ethereal extract, the acid was washed down with sodium carbonate solution and regenerated on reacidification. The acid (4 g.) passed over at 180°/0.1 mm. (Found: C, 62.36; H, 9.75. $C_{12}H_{22}O_4$ requires C, 62.58; H, 9.63 per cent).

The p-*bromophenacyl* derivative, prepared in the usual way, melted at 66-68° on twice crystallisation from alcohol. $[\alpha]_D^{18}$, -1°.3 (*c*=11.4 mg./c.c. in chloroform). (Found: C, 53.99; H, 5.27. $C_{28}H_{32}O_6Br_2$ requires C, 53.86; H, 5.17 per cent).

The acid was ketonised in the same manner and the semicarbazone was obtained, m. p. 132-36°. This on two crystallisations from methyl alcohol melted at 137-39° and showed no depression in m. p with the semicarbazone melting at 136-38°, described before. The melting point showed a tendency to rise on repeated crystallisation as in the previous case.

Ethyl 2-Methyl-5-isopropylcycloheptanone-7-carboxylate (XVIII).—sodium (1.5 g.) was dissolved in alcohol (25 c.c.) and cooled in a freezing mixture. Ethyl oxalate (11 g.) was added. The solution was cooled to -15° and to this was added the similarly cooled methyl*iso*propyl*cyclo*heptanone (8.4 g.) in two portions in the course of half-an-hour. The solution became yellowish and it was allowed to stand at -10° for 2 days. Next it was decomposed with ice and H_2SO_4(dil.) and the separated oil was taken up in ether. The ethereal solution was washed with sodium bicarbonate solution. The residue left on evaporation of the solvent was slowly heated in vacuum (50 mm.) after addition of boric acid (10 mg.). The temperature was raised from 130° to 170° in the course of 4 hours. Excess boric acid should not be used to avoid polymerisation. Next the temperature was raised to 195° and kept thereabout for half-an-hour and the pressure was adjusted to 30 mm. Finally it was distilled at 19 mm. when a yellow oil passed at 160-67°/19 mm., yield 8 g. On redistillation, it passed over at 163-67°/19 mm. or at 105-107°/0.2 mm. as a colorless oil, yield 7 g. (60%). Ferric chloride coloration in alcoholic solution was greenish blue. (Found: C, 69.23; H, 9.8. $C_{14}H_{24}O_3$ requires C, 69.96; H, 10.07 per cent).

Ethyl 1-Keto-3-methyl-6-isopropylsuberate (XII).—To sodium (2.4 g.), dissolved in absolute alcohol (50 c.c.) and cooled in a freezing mixture, was added a cooled mixture of menthone (15.4 g.) and ethyl oxalate (14.5 g.). The mixture was kept at 0° for 2 days when the colour of the solution became red. It was poured into ice-cold dilute sulphuric acid and the separated oil was taken up in ether. The residue after removal of the solvent was hydrolysed with a solution of KOH (28 g.) in methanol (250 c.c.) for 2 hours. Next it was diluted and the methanol removed on the steam-bath. On cooling it was extracted with ether to remove menthone, and the acidic fraction was isolated on acidification. The acidic fraction was thoroughly dried and esterified with a mixture of alcohol (35 c.c.) and H_2SO_4 (5 c.c.) for 16 hours.

It was diluted with water and extracted with ether and the ethereal solution was washed with a relatively concentrated solution of sodium carbonate, washed with water, dried and distilled. The keto-ester passed over at 127-30°/0.03 mm., yield 4.9 g (14%). It gave a bluish violet coloration with alcoholic ferric chloride solution. (Found: C, 64.04; H, 9.38. $C_{16}H_{28}O_5$ requires C, 63.97; H, 9.40 per cent).

Ethyl 1-Hydroxy-3-methyl 6-isopropylsuberate (XIII).—The above keto-ester (3.2 g.) was hydrogenated in acetic acid (15 c.c.) with platinum oxide catalyst (0.2 g.). The hydrogenation was complete in two hours (350 c.c.). The product was obtained at 120-22°/0.02 mm. in a quantitative yield. (Found: C, 63.68; H, 9.87. $C_{16}H_{30}O_5$ requires C, 63.54; H, 10.0 per cent).

Ethyl 1-Chloro-3-methyl-6-isopropylsuberate (XIV).—The above hydroxy-ester (14 g.) was mixed in the cold with PCl_5 (10 g.). In the beginning there was a violet coloration which vanished after a few minutes. After two hours it was decomposed with ice and extracted with ether. Acidic impurities were removed with sodium carbonate solution. The chloro-ester was distilled when it passed over at 115-20°/0.1 mm., yield 6 g. There was a residue (3 g.) in the flask. The alkaline wash was acidified and the acidic product was collected and mixed with the residue from the flask and treated as described afterwards. The chloro-ester was redistilled and the middle fraction was analysed. (Found: C, 59.96; H, 9.03. $C_{16}H_{29}O_4Cl$ requires C, 59.89; H, 9.11 per cent).

Ethyl 3-Methyl-6-isopropylsuberate (XV).—The chloro-ester (6 g.) in acetic acid (50 c.c.) was refluxed with zinc dust (6 g.) for 6 hours. On working up in the usual way, the desired ester distilled at 116-20°/0.1 mm., yield 4.3 g. (Found: C, 67.11; H, 10.29. $C_{16}H_{30}O_4$ requires C, 67.09; H, 10.59 per cent).

3-Methyl-6-isopropylsuberic Acid (XVI).—The above ester (4.2 g.) was refluxed for 12 hours with a solution of KOH (5 g.) in methanol (25 c.c.). The free acid (2.9 g.) was finally isolated on distillation; b.p. 175-80°/0.1 mm. (Found: C, 62.05; H, 9.48. $C_{12}H_{22}O_4$ requires C, 62.58; H, 9.63 per cent).

The p-*bromophenacyl* derivative, prepared in the usual way, crystallised from alcohol, m.p. 72-74°. (Found: C, 53.72; H, 5.03; $C_{28}H_{32}O_6Br_2$ requires C, 53.86; H, 5.17 per cent).

The residue from the distillation of the chloro-ester was refluxed with HI and red phosphorus, as described before, and a further quantity of the dibasic acid was obtained, which analysed as follows. (Found: C, 62.53; H, 9.52. $C_{12}H_{22}O_4$ requires C, 62.58; H, 9.63 per cent). The p-*bromophenacyl* derivative (m. p. 72-74°), prepared from the above acid, showed no depression with the derivative described before.

4 Methyl-7-isopropylsuberone (XVII).—The above acid (4.8 g.) was converted into thorium salt and the latter on dry distillation afforded a distillate (2.6 g.). This on redistillation passed over at 99-102°/12 mm. The semicarbazone, prepared in the usual way, melted at 120-22°, on thrice crystallisation from methanol. (Found: C, 63.91; H, 10.32. $C_{12}H_{23}ON_3$ requires C, 63.96; 10.29 per cent).

This sample was repeatedly crystallised from methanol, when a small amount of crystals melting at 125-27° with previous softening at 122° was isolated.

The semicarbazone (1.6 g., m. p. 120-22°) was decomposed with steam in presence of oxalic acid and the ketone (0.9 g.) was obtained, boiling at 100-102°/12 mm. $[\alpha]_D^{20}$, -20°.2 (13.8 mg./c.c. in alcohol); η_D^{20}, 1.4590; d^{20}, 0.9082. (Found: C, 78.32; H, 12.11. $C_{11}H_{20}O$ requires C, 78.51; H, 11.98 per cent).

These experiments were carried out in the chemical laboratories of E. T. H., Zürich, Switzerland and the author places on record his grateful thanks to Prof. Plattner and Dr. Fürst for their kind help and encouragement and also for the laboratory facilities. Thanks are also due to the University of Calcutta for the award of a Ghosh Travelling Fellowship in Science.

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CONSTITUENTS OF *CENTALLA ASIATICA*. PART III. EXAMINATION OF THE INDIAN VARIETY

By S. C. Bhattacharyya

The components of the Indian variety of the plant *Centalla asiatica* have been examined. The main triterpenic constituent, indocentoic acid, appears to be isomeric with centoic acid, isolated from the Ceylonese variety.

In previous communications of this series (this *Journal*, 1956, **33**, 579, 630 ; *Nature*, 1949, **163**, 258, 260) the isolation of a triterpenoid glycoside and three polyhydroxy triterpenic acids- centic, centoic and centellic acids- from the Ceylonese variety of *Centalla asiatica* has been described and the structures of the triterpenes discussed. In the present communication the results of examination of the Indian variety of the plant have been recorded.

The constituents of the plants were like those of the Ceylonese variety. It was also found to contain salts, sugars, essential oils and pectin. The most characteristic constituent in this case also is, however, a mixture of triterpenic acids which can be isolated and initially purified by following exactly the same procedure as adopted for the Ceylonese variety. The ultimate aqueous mother-liquor, left after precipitation of the triterpenes, has been found to contain a considerable amount of a water-soluble glycoside which is also a sugar-ester, like centelloside and asiaticoside (vide Parts I and II, *loc. cit.*) and, like these, could be hydrolysed easily by both acid and alkali. The presence of sugar-ester type glycosides appears to be a characteristic for *C. asiatica*.

In the present case the individual triterpenic constituents were separated through the crystallisation of their brucine salts and were divided into three distinct and two unspecified minor fractions (vide Experimental). Of these, only the major triterpenic constituent, "*indocentoic acid*", and the water-soluble glycoside, "*indocentelloside*", were examined in some details.

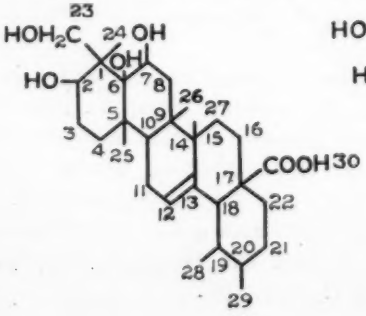
The equivalent weight of indocentoic acid, as determined by micro-titrations, when correlated with elemental analysis, clearly indicates that like centoic acid, it has the same molecular formula $C_{30}H_{48}O_6$, which has been further confirmed by equivalent weight and analysis of the acetyl and other derivatives. It responds to the usual colour tests for triterpenes.

Indocentoic acid does not react with any carbonyl reagent and does not show any U. V. absorption. Like centoic acid, the carboxyl group in it is also tertiary, as the crystalline methyl ester, obtained through reaction with diazomethene, is resistant towards hydrolysis. The presence of a double bond was indicated by colour reaction with tetranitromethane, but, as expected, it was also resistant towards hydrogenation. Formation of bromolactone reveals the usual γ-δ-position of the double bond with respect to the carboxyl group (Winterstein and Hammerle, *Z. physiol. Chem.*, 1931, **199**, 56, 64, 74 ; Haworth, *Ann. Report*, 1939, 338).

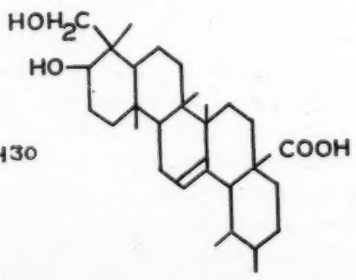
In the presence of an acidic catalyst, the methyl ester of indocentoic acid condensed with two molecules of acetone, forming a crystalline di-*iso*propylidene derivative. This indicates that all the four remaining oxygen functions in its molecule are in the form of hydroxyl groups. With pyridine and acetic anhydride and also with sodium acetate and acetic anhydride, under usual conditions, indocentoic acid was converted into a diacetyl derivative, the remaining two hydroxyl groups being resistant towards acetylation. In this respect indocentoic acid differs from centoic acid and asiatic acid, both of which form triacetyl derivatives (Parts I and II, *loc. cit.*).

The presence of at least one primary hydroxyl group in indocentoic acid was indicated by the copper bronze test (Heywood and Kon, *J. Chem. Soc.*, 1939, 1125; Tsuda and Kitagowa, *Ber.*, 1938, **71**, 1604). But as the acid contains only two acetylable hydroxyl groups, one of which will be the usual secondary C_2-hydroxyl group, common for triterpenes, the remaining one must necessarily be the one and the only primary hydroxyl group present in its molecule, as primary hydroxyl groups occurring in triterpenes are usually acetylable. This conclusion could be further confirmed from the information given below.

Indocentoic acid contains an α-glycol linkage as shown by the consumption of one moleucle of sodium periodate. The same α-glycol linkage is also present in the methyl ester, diacetyl derivative and the diacetylated methyl ester. Both the resistant hydroxyl groups are therefore involved in the glycol linkage. The presence of glycol linkage in the diacetylated product further confirms the presence of four hydroxyl groups. The periodate scission product, obtained as above, gave tests for aldehyde. At least one of the hydroxyl groups involved in the α-glycol linkage is therefore a resistant secondary hydroxyl group, similar to that occurring in other triterpenes like sumaresinolic acid, echinocystic acid, quillaic acid, genin A, manila diol etc. (Jegar, "Fort. der. Chim. Org. Naturstoffe", 1950, pp. 24, 31, 32, 33, 46). The other hydroxyl group involved in the α-glycol linkage must also necessarily be a tertiary or a secondary hydroxyl group, as the triterpene structure excludes the possiblity of a resistant primary hydroxyl group taking part in the formation of an α-glycol linkage with another resistant secondary hydroxyl group, a conclusion which is also indicated as no formaldehyde is formed during oxidation. This finding further confirms the presence of only one primary hydroxyl group in indocentoic acid.



(I)



(II)

Dehydrogenation of indocentoic acid with selenium, carried out on a small scale, followed by chromatographic separation, indicates the usual dehydrogenation products.

From a critical interpretation of these results, it would appear that indocentoic acid is very similar to asiatic acid and centoic acid. It is isomeric with the latter (I) and may be expected to have the same basic α-amyrin skeleton.

In common with other triterpenes, indocentoic acid will also have an acetylable secondary hydroxyl group at C_2. This group, however, could not be a component part of the α-glycol linkage, as that would have required the presence of another secondary acetylable hydroxyl at C_3, similar to that present in asiatic acid (vide Part II, *loc. cit.*).

Irrespective of the position of the α-glycol linkage, composed of two non-acetylable hydroxyl groups, the primary hydroxyl group present in the acid must be located on C_{23} (or 24), as no other position of the same can explain the formation of the di-*iso*propylidene derivative which will be formed only by α- and β-glycols. This leads to the partial structure (II) for indocentoic acid. If the α-glycol linkage is located at "C_6-C_7", as in the case of centoic acid (I), the two acids will have the same structural formulae, differing, probably, in steric disposition of the hydroxyl groups. Location of the α-glycol linkage in indocentoic acid, however, is still uncertain.

The water-soluble glycoside, indocentelloside, has also been preliminarily examined. On hydrolysis it furnished reducing sugars and a triterpenic aglycone which on characterisation through its brucine salts was found to be identical with indocentoic acid.

EXPERIMENTAL

Unless otherwise stated, samples were usually dried to a constant weight at 100°-110°/1-2 mm. Equivalent weights were determined following the standard micro procedure in dilute alcoholic solution and always checked by simultaneous determination of the same for cholic acid.

The plant was collected in Assam, dried in the sun and then shipped to Cambridge for examination. Nearly six months passed after collection, before its chemical examination could be commenced.

For the isolation of the salts, sugars, essential oils and pectin, the same procedure as described in Part I (*loc. cit.*) was employed.

Triterpenes and Glycoside.—These were isolated from the alcoholic extract of the plant. The process was the same as described in Part I (*loc. cit.*). The extract after drying was found to contain less of waxy material as compared to the former variety. After extraction with petrol and processing through lead acetate-treatment etc., a pale yellow alcoholic solution was obtained as a final product. On concentration and dilution with water, it deposited a mixture of triterpenic acids (160 g. from 9 kg. of the plant). The aqueous mother-liquor contained indocentelloside.

Separation of the Acids through Brucine Salt.—The dried triterpene acids (160 g.) and brucine (128 g.) were dissolved in alcohol (2½ litres) and refluxed (charcoal, 20 g.) for 2 hours. After filtration the solution was left at 0° for 24 hours. The crystals of brucine salt (120 g., large plates) were collected and washed with ice-cold alcohol (300 c.c.). The mother-liquor on concentration and cooling furnished a second crop

which on recrystallisation provided about 11 g. of brucine salt ; the latter was added to the main crop. The combined amount after recrystallisation from alcohol three times afforded the brucine salt of indocentoic acid in the form of microscopically pure large plates, yield 60 g., $[\alpha]_D^{17}$, -77° (alcohol, c = 1.37%).

For the isolation of the free acid, the brucine salt, as obtained above, was decomposed with mineral acid in the usual way, and the free acid was further purified by reprecipitation from alcohol and dried to a constant weight ; $[\alpha]_D^{17}$, + 38°.6 (pyridine, c= 1.464%). In a preheated bath (22°), the acid melted at 272°, which was fairly reproducible. It developed a yellow colour with tetranitromethane and the usual cherry-red colour with $H_2SO_4-HNO_3$. (Found : C, 71.51 ; H, 9.82 ; equiv., 500.0, 497.0, 502.1. $C_{30}H_{48}O_6$ requires C, 71.39 ; H, 9.59 per cent. Equiv., 504.68).

Estimation of Glycol-linkage.—The same procedure as in the case of centoic acid was followed. Periodate consumed was 1.067 mole (calc. 1.0 mole). The scission product responded to various tests for aldehyde.

Diacetyl derivative.—Indocentoic acid (1 g.) was dissolved in anhydrous pyridine (15 c.c.) and acetic anhydride (5 c.c.) was added. The mixture was left at room temperature for 24 hours and then the acetyl derivative was isolated and worked up in the usual way. It could not be crystallised ; it shrank at 145° and formed a glass at 150°. (Found : C, 69.40 ; H, 8.73 ; equiv., 591.6, 591.6, 590.2. $C_{34}H_{52}O_8$ requires C, 69.36 ; H, 8.90 per cent. Equiv., 588 76).

The same acetyl derivative was obtained by refluxing indocentoic acid with acetic anhydride, glacial acetic acid and freshly fused sodium acetate for 3 hours and then working up the product. The derivative shrank at 140° and formed a glass at 150°. (Found : C, 69.20 ; H, 8.51. $C_{34}H_{52}O_8$ requires C, 69.36 ; H, 8.90 per cent). Both the diacetyl derivatives gave positive test with Feigl's periodate-silver nitrate test, indicating the presence of glycol linkage (Feigl, "Spot Tests", 1946, p. 327).

Methyl Ester of Indocentoic Acid.—To the powdered acid (5 g.), suspended in anhydrous ether (100 c.c.), a distilled solution of diazomethane was added in excess. Within a short time the entire amount of the acid went into solution. After a few hours at room temperature, the methyl ester started crystallising out, and after 24 hours the entire mass had crystallised ; yield 4.5 g. It could be recrystallised from ether or acetone-methanol mixture, m.p. 173 - 75°. (Found : C, 72.75 ; H, 9.60. $C_{31}H_{50}O_6$ requires C, 71.78 ; H, 9.72 per cent). A better analysis for carbon could not be obtained. The ester showed characteristic periodate reaction for α-glycol. The scission product gave tests for the aldehyde function.

*Di-iso**propylidene-methyl Ester.*—The crystalline methyl ester (1 g.) was dissolved by warming in acetone (10 c.c.) ; HCl. (conc., 4 drops) was added and the mixture left at room temperature. Within a short time the *iso*propylidene derivative crystallised in fine needles. The crystals were collected (0.6 g.) after a few hours and recrystallised from 5 c.c. of acetone, m.p. 213°. (Found : C, 74. 12 ; H, 10.0. $C_{37}H_{58}O_6$ requires C, 74.21 ; H, 9.76 per cent).

Bromolactone of Indocentoic Acid.—This preparation was examined only from the qualitative point. Following the same procedure as in the case of centoic acid, indocen-

toic acid (0.5 g.) gave about 0.3 g. of the neutral bromolactone containing bromine, as indicated by qualitative tests.

Detection of Primary Alcoholic Group.—Exactly the same procedure, as employed in the case of centoic acid in Part II (*loc. cit.*), was used. Formaldehyde formed during the reaction was characterised as its dimedone derivative, m.p. and mixed m.p. 189°.

Dehydrogenation of Indocentoic Acid.—The acid (5 g.) and selenium (6 g.) were used for the experiment. Initially the same procedure as in the case of centoic acid was used. The ethereal solution, obtained after extraction of the dehydrogenation product, was filtered and then by treatment with dilute alkali (2 × 25 c.c.) was divided into (*i*) phenolic fraction and (*ii*) non-phenolic fraction. The alkaline extract on acidification and extraction with ether gave the free phenol (4 mg.) which was qualitatively characterised through colour reaction with diazonium salt.

The non-phenolic portion after removal of the solvent was dissolved in benzene (10 c.c.) and chromatographed on a column of alumina (100 g., grade o). The column was developed with light petroleum-benzene. Five fractions were collected. Removal of solvents gave the corresponding products from :

(*i*) 300 c.c. of 3 : 1 petroleum-benzene ; 0.7 g. oil ; came out through the column very rapidly.
(*ii*) 250 c.c. of 3 : 1 petroleum-benzene ; 60 mg., oil
(*iii*) 250 c.c. of 2 : 1 do ; 100 mg., crystals
(*iv*) 250 c.c. of 2 : 1 do ; 80 mg., oil and crystals
(*v*) 1000 c.c. of benzene ; 100 mg., crystals.

Fractions (*i*) and (*ii*) formed a picrate which after three crystallisations from alcohol melted at 120° and it was possibly the picrate of 1 : 7-dimethylnaphthalene, m.p. 121°. Analysis also supported this. (Found : C, 56.32 ; H, 4.06. $C_{18}H_{15}O_7N_3$ requires C, 56.10 ; H, 3.92 per cent). Formation of 1 : 7-dimethylnaphthalene is possible from triterpenes. Sapotaline could not be isolated in quantity. The other fractions on crystallisations from benzene-petroleum, followed by micro-vacuum sublimation (bath temp. 260°/10^{-4} mm.) gave shining crystals, m.p. 298°. The melting and sublimation temperatures were comparable to those of 1 : 8-dimethylpicene (m.p. 305°, corr.) or 1 : 7 : 8-trimethylpicene (m.p. 309°, corr.).

Indocenteiloside.—The ultimate mother-liquor, obtained after removal of triterpene, was acidified and then saponified by refluxing for a short time. The acidic aglycone (4 g. from 1 kg. of the dried plant) was converted into brucine salt, which was purified by repeated crystallisations from alcohol in microscopically pure, large plates similar to that of centoic acid but having no sharp melting point. It started softening at 145° and then slowly melted into a glass ; $[\alpha]_D^{17}$, −70° (EtOH, $c = 1.3\%$) same as the brucine salt of indocentoic acid. Due to lack of any sharp melting point, identity through mixed melting point was not dependable ; microscopic purity and optical rotation were to be preferred.

Other Miscellaneous Constituents.—The mother-liquor, left after the first cryatallisation of the brucine salt of triterpenic acid mixture, was processed partly according to the triangular scheme with the following broad results :

(*i*) Amorphous brucine salt (about 40 g.). The free acid from it formed a crystalline potassium salt and could be purified through that derivative. The acid, thus obtained, formed a crystalline brucine salt.

(*ii*) A dark mother-liquor, containing a considerable amount of highly soluble brucine salt, somewhat similar to that of centellic acid.

(*iii-iv*) Two minor unspecified fractions. These fractions were not further examined.

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ESTIMATION OF COBALT BY BENZIMIDAZOLE

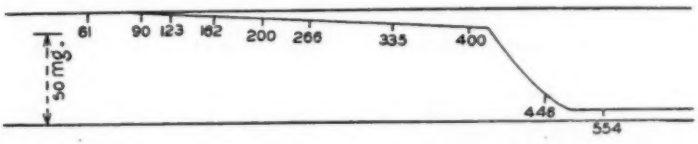
By S. P. Ghosh and H. M. Ghose

A new method for the estimation of cobalt has been established. Cobalt is precipitated as $Co(C_7H_5N_2)_2$ by aqueous benzimidazole at p_H 10. The precipitate is dried at 105° and weighed as such. The compound contains 20.12% cobalt. Cobalt can be estimated by this method in the presence of barium and calcium.

It has been reported by one of us (this *Journal*, 1951, **18**, 710) that cobalt^{II} forms with benzimidazole an unusually stable complex of brilliant violet colour. The complex is of the same type as that formed by nickel with dimethylglyoxime. It is sparingly soluble in water, and, when dried at 105°, has the constant composition, $Co(C_7H_5N_2)_2$, containing 20.12% cobalt. The precipitation is complete at p_H 10 and the precipitate is made easily filtrable in presence of a small amount of potassium sulphate.

The cobalt complex was subjected to thermogravimetric analysis to ascertain the proper temperature for drying. From the thermolysis graph (Fig. 1) it can be seen that the complex starts decomposing at about 100°. The amount of decomposition is extremely small till 120° for a macro-scale analysis; so a drying temperature of 105° is recommended to minimise the time of drying.

Fig. 1



In order to compare this method with the standard electrolytic and "cobalt sulphate" methods, a statistical analysis of the data was made, and it was found out to be equally efficient. As the precipitation is done at p_H 10, all elements, forming insoluble hydroxide, must be absent. Common anions were found not to interfere when not present in large excess. Estimation of cobalt can be more easily done by this method than the two standard methods, referred to above. The reagent can also be very easily prepared.

Experimental

Benzimidazole was prepared according to the method of Wundt (*Ber.*, 1878, **11**, 826). *o*-Phenylenediamine (54 g.) was heated with 90% formic acid (32 c.c.) on a water-bath for 2 hours. The mixture was then treated with 10% caustic soda till alkaline. The liberated benzimidazole was filtered and purified by recrystallisation from hot water, m. p. 171-72°. Approximately 1% solution of the reagent was obtained by dissolving the requisite amount in warm distilled water and filtering off any insoluble residue. Such a solution was found to keep well for over 4 weeks.

A standard cobalt solution was prepared by dissolving cobalt chloride of analytical grade (B. D. H.) in water. The stock solution was standardised both by electrodepositing the cobalt and by converting the chloride into sulphate and weighing as anhydrous cobalt sulphate.

For estimation, a known amount of the standard cobalt solution was taken in a 500 c.c. Jena beaker and the volume was made up to about 150 c.c. with water. To the solution was added 2 g. of A. R. potassium sulphate. The reagent solution was then added in 100 % excess. The mixture was rendered alkaline (p_H 10, tested with p_H paper) with dilute ammonia. It was thoroughly stirred and digested for ½ an hour on the water-bath. The precipitate was then filtered in a sintered glass Gooch crucible of medium porosity (Jena 1 G 3). The precipitate was thoroughly washed with warm water till free of chloride, and dried in an air-oven at 105° to a constant weight. The results of analysis are shown in Table I.

TABLE I

Co taken.	Co found.	Diff.	Co taken.	Co found.	Diff.
0.0630 g.	0.0628 g.	− 0.0002	0.0218 g.	0.0221 g.	+ 0.0003
0.0605	0.0607	+ 0.0002	0.0169	0.0168	− 0.0001
0.0605	0.0606	+ 0.0001	0.0169	0.0167	− 0.0002
0.0327	0.0328	+ 0.0001	0.0121	0.0118	− 0.0003
0.0285	0.0283	− 0.0002	0.0121	0.0118	− 0.0003

It was found that cobalt could be correctly estimated by this method when present between the limit of 63 and 12 mg.

Following is the statistical analysis of the above data :

$$\bar{x} = (-0.0013 + 0.0097)\ 1/10 = -0.00006.$$

To find the standard deviation, s,

$$(n-1)\,s^2 = \Sigma x_i^2 - n\bar{x}^2$$
$$= 0.00000046 - 0.000000036$$
$$= 0.000000424$$

or
$$s^2 = 0.00000004711$$
$$s = 0.000215 \text{ correctly.}$$

If the method were to give correct result, we have $\mu = 0$.

Now
$$t = \frac{|\bar{x} - \mu|}{s}\sqrt{n} = \frac{0.00006 \times 3.162}{0.000215}$$
$$= 0.8824 \text{ on 9 degrees of freedom.}$$

The probability that this value of t will be exceeded numerically, in random analysis, is more than 0.50 ; the value is thus not significant. Hence the method is equally suitable as the methods for standardisation. Any error is due to chance factor.

Estimation of Cobalt in presence of Barium and Calcium.—Here ammonia used for the precipitation was freshly prepared to avoid the precipitation of carbonate.

TABLE II

Co taken.	Taken.	Found.	Co found.
0.0242 g.	Ba 0.0122 g.	Ba 0.0121 g.	0.0243
0.0242	Ca 0.0093	Ca 0.0091	0.0243

Thanks of the authors are due to the Council of Scientific and Industrial Research for financial help. Thanks are due to Prof. A. K. Majumdar of Jadavpur University by whose courtesy the thermolysis graph was done in Prof. C. Duval's laboratory at Paris. Thanks are also due to Dr. D. N. Lal for his interest in the statistical analysis.

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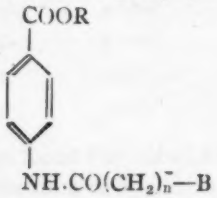
SEARCH FOR NEW LOCAL ANAESTHETICS. PART II

By I. Sen Gupta, K.S. Narang, O. P. Vig and P. C. Bansal

Several piperidino-, diethylamino- and morpholino-acetyl and -propionyl derivatives of alkyl *p*-aminobenzoates have been synthesised to study their local anaesthetic activity.

A series of alkyl *p*-aminobenzoates, when tested against goldfish, showed local anaesthetic activity, and both the activity and toxicity of the compounds increased with the increasing molecular weight of alkyl group (Adams *et al.*, *J. Amer. Chem. Soc.*, 1926, **48**, 1758). Esterification of *p*-aminobenzoic acid by various tertiary amino-alkanols led to the synthesis of procaine and its analogues, showing high local anaesthetic activity (Einhorn and Uhlfelder, *Annalen*, 1909, **371**, 131; Vliet and Adams, *J. Amer. Chem Soc.*, 1926, **48**, 2158; Adams *et al.*, *ibid.*, 1937, **59**, 2248). Since basic anilides having lypolytic and hydrophillic moieties also showed local anaesthetic activity (Lofgren, *Chem. Abs.*, 1937, **31**, 7854; Gaind *et al.*, this *Journal*, 1940, **17**, 400, 600), it was thought of interest to convert the amino group in alkyl *p*-aminobenzoates into a basic anilido group, yielding compounds of the general formula (I).



(I)

B = Diethylamino, piperidino and morpholino.

n = 1 or 2.

R = Propyl, *iso*propyl and *n*-butyl.

These compounds have an ester and a basic anilido group, and the acylation of amino group is expected to decrease the toxicity. The presence of propyl, *iso*propyl and *n*-butyl group in the ester part well balances the activity and the toxicity in the molecule.

For the preparation of compounds of type (I), alkyl *p*-aminobenzoate was treated with chloroacetyl chloride or *β*-chloropropionyl chloride. The resulting chloroacylated compound was then condensed with a secondary amine in absolute alcohol. The bases were finally converted into their hydrochlorides. Some of the hydrochlorides being uncrystallisable sticky masses, the bases were converted into the hydrobromides.

Experimental

*iso*Propyl p-(*Chloroacetamido*)-*benzoate*.—Chloroacetyl chloride (11.3 g.) in dry benzene (30 c c.) was gradually added to *iso*propyl *p*-aminobenzoate (17.9 g.) in dry benzene (50 c.c.). The reaction mixture was heated under reflux for 4 hours. Benzene was removed by distillation and the residue washed first with dilute HCl and then with sodium bicarbonate solution, followed twice with water. The product was crystallised from petroleum ether (b.p. 60°-80°) in small needles, m.p. 100°. (Found : N, 5.19; Cl, 13.95. $C_{12}H_{14}O_3NCl$ requires N, 5.47; Cl, 13.9 per cent).

TABLE I

Compounds.	Crystallised from.	M.P.	Mol. formula.	Analysis. Found.	Calc.
*iso*Propyl-*p*-(diethylamino-acetamido)-benzoate-HCl	Absolute alcohol	206°	$C_{16}H_{25}O_3N_2$ HCl	N: 8.75%	8.56%
*iso*Propyl-*p*-(N-morpholino-acetamido)-benzoate-HCl	Acetone	220°	$C_{16}H_{22}O_4N_2$.HCl	N: 7.77	8.17
				Cl: 9.7	10.3
*iso*Propyl-*p*-(β-chloropropinamido)-benzoate	Alcohol	125°	$C_{13}H_{16}O_3NCl$	C: 58.27	57.89
				H: 6.15	5.93
				N: 5.16	5.19
*iso*Poropyl-*p*-(β-N-piperidino-propionamido)-benzoate	Pet. ether (40°-60°)	78°	$C_{18}H_{26}O_3N_2$	N: 8.11	8.6
*iso*Propyl-*p*-(β-diethylamino-propionamido)-benzoate-HBr	Acetone	188°	$C_{17}H_{27}O_3N_2$.HBr	N: 7.42	7.21
*iso*Butyl-*p*-(chloroacetamido)-benzoate	Pet. ether (80°-100°)	115°	$C_{13}H_{16}O_3NCl$	N: 5.2	5.2
				Cl: 13.32	13.17
*iso*Butyl-*p*-(N-piperidino-acetamido)-benzoate	Pet. ether (40°-60°)	86°	$C_{18}H_{26}O_3N_2$	N: 8.78	8.8
Hydrochloride of the above base	Acetone-ether	228°	...	...	...
*iso*Butyl-*p*-(diethylamino-acetamido)-benzoate-HCl	Absolute alcohol	153°	$C_{17}H_{26}O_3N_2$.HCl	N: 8.1	8.17
				Cl: 10.3	10.36
*iso*Butyl-*p*-(N-morpholino-acetamido)-benzoate	Dil. alcohol	90°	$C_{17}H_{24}O_4N_2$	N: 8.7	8.75
*iso*Butyl-*p*-(β-chloropropionamido)-benzoate	Pet. ether (60°-80°)	112°	$C_{14}H_{18}O_3NCl$	N: 5.38	4.96
*iso*Butyl-*p*-(β-N-piperidino-propionamido)-benzoate	Alcohol	77°	$C_{19}H_{28}O_3N_2$	N: 7.97	8.42
Hydrochloride of the above base	Acetone-ether	210°		...	...
*iso*Butyl-*p*-(β-diethylamino-propionamido)-benzoate	Dil. acetone	87°	$C_{18}H_{28}O_3N_2$	N: 8.25	8.75
Hydrobromide of the above base	Acetone-ether	201°		...	...
*iso*Butyl-*p*-(β-N-morpholino-propionamido)-benzoate	Pet. ether (60°-100°)	110°	$C_{18}H_{26}O_4N_2$	N: 8.25	8.36
Hydrochloride of the above base	Acetone-ether	218°		...	...
n-Butly-*p*-(chloro-acetamido)-benzoate	Pet. ether (40°-60°)	80°	$C_{13}H_{16}O_3NCl$	N: 5.36	5.2
				Cl: 12.65	13.17
n-Butyl-*p*-(N-piperidino-acetamido)-benzoate	Alcohol	88°	$C_{18}H_{28}O_3N_2$	N: 8.4	8.75
Hydrochloride of the above base	Acetone-ether	192°		...	...
n-Butyl-*p*-(diethylamino-acetamido)-benzoate-HBr	Do	135°	$C_{17}H_{26}O_3N$.HBr	N: 7.25	7.23
				Br: 20.0	20.5
n-Butyl-*p*-(N-morpholino-acetamido)-benzoate	Pet. ether (40°-60°)	66°	$C_{17}H_{24}O_4N_2$	N: 8.65	8.75
Hydrochloride of the above base	Acetone-ether	190°		...	...
n-Butyl-*p*-(β-chloropropionamido)-benzoate	Dil. alcohol	93°	$C_{14}H_{18}O_3NCl$	C: 58.78	59.25
				H: 6.26	6.34
				N: 4.93	4.93
n-Butyl-*p*-(β-N-piperidino-propionamido)-benzoate	Pet. ether (40°-60°)	62°	$C_{19}H_{28}O_3N_2$	N: 8.35	8.42
Hydrochloride of the above base	Acetone-ether	208°		...	...

iso*Propyl* p-(N-*piperidino-acetamido*)-*benzoate*.—A mixture of piperidine (1.7 g.), *iso*propyl *p*-(chloroacetamido)-benzoate (2.55 g.) in 2:1 molecular proportion in absolute alcohol (40 c.c.) was refluxed on a water-bath for 5 hours. Alcohol was recovered by distillation and the residue dissolved in dilute HCl. It was filtered and the filtrate made alkaline with ammonium hydroxide solution. The base was collected, washed with water and crystallised from dilute alcohol. It was recrystallised from pertoleum ether (40°-60°) in long needles, m.p. 80°, yield 2.6 g. (Found: N, 8.75. $C_{17}H_{24}O_3N_2$ requires N, 9.21 per cent).

Hydrochloride of the above Base.—The base (2 g.) was dissolved in absolute alcohol (20 c.c.) and the solution saturated with dry HCl. Alcohol was removed by distillation and the residue crystallised from acetone-ether mixture, m.p. 235-36°. The other analogues synthesised in a similar manner are shown in Table I.

Hydrochloride of *iso*butyl *p*-(N-piperidino-acetamido)-benzoate was tested for local anaesthetic activity at the Central Drug Research Institute, Lucknow. It showed no surface anaesthesia when applied to the cornea of guineapigs in 3% solution. However, for intradermal anaesthesia in 2% solution in normal saline, the action lasted for 60 minutes. It produced inflammatory reaction also. The compounds are being further studied for their pharmacological activity.

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PAPER CHROMATOGRAPHIC STUDIES OF SOME NATURAL COUMARINS

By D. P. Chakraborty and P. K. Bose

Chromatographic technique has been applied for the separation and identification of 12 natural coumarins. From the results it appears that coumarins are to some extent separable and water appears to be the most suitable solvent for the purpose.

Partition paper chromatography has in recent years proved very useful in the detection, identification and separation of organic compounds of plant or animal origin. The method is also valuable in judging the homogeneity of compounds.

The detection of coumarins by means of this technique is of recent interest (Sevendson, *Pharm. Acta Helv.*, 1952, **27**, 44; Riedel and Neugebaur, *Monatsh.*, 1952, **83**, 1083). In course of studies of naturally occurring polyphenols involved in the enzymatic browning by potato polyphenolase, Swain (*Biochem. J.*, 1953, **53**, 200) applied this method for the detection of minute quantities of coumarins. In course of our work on the isolation and identification of small quantities of coumarins present in plant materials, need was felt for a further study of paper chromatography of some natural coumarins.

For this purpose, twelve natural coumarins, which we could secure, were chosen. These are listed in Table I.

Table I

Name.	*Occurrence.
1. Ayapin	*Eupatorium ayapana*, Vent.
2. Bergapten	*Citrus aurantifolia* (Christm.), Swingle.
3. Byakangelicin	*Angelica glabra*, Makino.
4. Coumarin	*Anthoxanthum odoratum*, Linn.
5. Ferulin	*Ferula alliacea*, Boiss.
6. Limettin	*Citrus aurantifolia* (Christm.), Swingle (Khastagir, this *Journal*, 1947, **24**, 421).
7. Luvangetin	*Luvanga scandens*, Ham.
8. Marmesin	*Aegle marmelos*, Correa.
9. Marmin	*Aegle marmelos*, Correa. (Chatterjee & Chowdhury, *Naturwiss.*, 1955, **42**, 512).
10. Murrayin	*Murraya exotica*, Linn.
11. Pimpinellin	*Pimpinella saxifraga*, Linn.
12. Seselin	*Seseli indicum*, W & A.

* Dean, Fortschitte der Chemie organischer Naturstoffe", 1952, IX, pp. 235-291.

The above coumarins were subjected to paper chromatography by the uni-dimensional ascending technique with a number of solvent systems of which twenty one, which ensured reproducible results, were finally chosen. The solvent systems are mentioned in Table II.

TABLE II

1.	Water		
2	Methanol-acetic acid-water	...	16 : 3 : 1
3.	Methanol-formamide-water	...	1 : 2 : 7
4.	Mathanol-formic acid-water	...	16 : 3 : 1
5.	Methanol-ammonia*-water	...	6 : 1 : 3
6.	Water-dioxane	...	9 : 1
7.	Do	...	1 : 3
8.	Ethyleneglycol-water	...	1 : 24
9.	Do	..	1 : 9
10.	Pyridine-water	...	3 : 97
11.	Pyridine-ammonia*-water	...	1 : 2 : 7
12.	Formamide-ammonia*-water	...	2 : 2 : 7
13.	Acetone-petroleum ether-water	...	5 : 3 : 4 (lower phase)
14.	Petroleum ether-benzene-water	...	15 : 1 : 5
15.	Do	...	10 : 1 : 3
16.	*iso*Propanol-ammonia*-water	...	3 : 2 : 5
17.	*iso*Propanol-ammonia*	...	10 : 1
18.	*n*-Butanol (saturated with water)		
19	*n*-Butanol-water-acetic acid	...	4 : 1 : 1
20.	Acetic acid	...	10%
21.	*tert.*-Butanol-ammonia*	...	9 : 1

*Aqueous ammonia solution of sp. gr. 0.91.

EXPERIMENTAL

Method.—A solution of the coumarin (5 mg. in 2 c.c. ethanol) was, as a rule, used. Where the solubility was low, a saturated ethanolic solution was employed. The primary spots, delivered from a micro-pipette on to the filter paper, represented approximately 10 μl of the solution or 0.025 microgram of the substance. The arrangement and procedure were the same as those described by Burma and Banerjee (this *Journal*, 1951, **28**, 135). Whatman filter paper No. 1 was used. Solvents used were of the purest quality available. In the cases of mixed immiscible solvents, the upper phase was used except where mentioned otherwise (*vide e.g.*, solvent system 13). The experiments were conducted at room temperature (25°-31°). Each experiment was repeated 3 to 6 times under approximately the same conditions.

The spots in the chromatogram were observed under the ultraviolet light (Chromatolite 2537Å). Treatment of the paper with ammonia vapour or 2*N*-NaOH solution intensified the fluorescence under the ultraviolet light. The R_f values are recorded in Table III, while Table IV shows the nature of fluorescence observed with different spray reagents.

The spots were usually elongated. Trailing of spots was generally noticed with water as the solvent. This effect was most marked in the case of luvangetin with solvent systems 8 and 9, so that no R_f value could be calculated. The effects were generally much less in acidic solvents. Seselin and pimpinellin gave two spots each in solvent system 11. This abnormality is believed to be due to partial opening of the lactone ring in presence of the basic solvent.

After having determined the R_f values of individual coumarins in the different solvent systems, attempts were made to separate and identify each of the constituents from a mixture of all the twelve coumarins.

The results of experiments with mixtures of coumarins are shown in Table III. It is evident that ferulin, bergapten and murrayin could be separated and identified in solvent systems, 1 and 6. In the solvent system 1, four other distinct spots were also noticed. These had R_f values 0.38, 0.49, 0.55, 0.67 respectively, and proved (from observations of the nature of fluorescence) to be due to mixtures of coumarins having similar R_f values.

TABLE III

R_f values of coumarins in different solvents.

Solvent No. / Coumarins.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Ayapin	0.48	0.73	0.76	0.79	0 68	0.63	0.96	0.50	0.56	0.59	0 72	0.74
Bergapten	0.20	0.74	0.65	0.68	0.63	0.41	0.98	0.17	0.26	0.32	0.78	0.53
Byakangelicin	0.54	0.75	0.85	0.69	No spot	0.71	No spot	0.55	0.62	0.67	0.72	No spot
Coumarin	No spot	No spot	No spot	No spot	Do	No spot	Do	No spot	No spot	No spot	0.89	0.91
Ferulin	0.0	0.76	Do	0.95	0.84	0.0	0.93	Do	Do	Do	0.83	No spot
Limettin	0.36	0.73	0.76	0.68	0.73	0.57	0.98	0.47	0.4	0.56	0.76	0.65
Luvangetin	0.46	0.79	0.81	0.72	0.82	0.69	0.68	Very long	dragging.	0.86	0.89	0.76
Marmesin	0.66	0.76	0.90	0.89	0.76	0.77	0.95	0.67	0.70	0.78	0.83	0.81
Marmin	0.64	0.78	0.91	0.90	0.71	0.76	0.97	0.65	0.73	0 73	0.79	0.79
Murrayin	0.76	0.61	0.95	0.74	0.72	0.82	0.91	0.75	0.77	0.81	0.92	0.87
Pimpinellin	0.38	0.79	0.80	0.89	0.77	0.61	0.97	0.43	0.54	0.59	0.76	0.72
Seselin	0.43	0.79	0.84	0.90	0.79	0.62	0.97	0.44	0.54	0.55	0.79	0.76
Mixture	0.00	0.59	Over lapp-	0.75	0.69	0.00	0.90	Over lapp-	0.26	0.28	0.71	0.59[a]
	0.18	0.69	ing fluores-	0.84	0.77	0.41[a]	0.98	ing fluo-	0.32	0.44	0.84	0.79
	0.37	0.82	cent zones	0.97	0.83	0.62		rescent	0.52	0.57	0.92	
	0.49					0.70		zones	0.58	0.83		
	0.55					0.74			0.72			
	0.67					0.81						
	0.77[a]											
Expt. temp.	30°±1°	28.5°±1°	30°±1°	29.5°±1°	29.5°±1°	30°±1°	30°±1°	29.5°±1°	30°±1°	29.5°±1°	29.5°±1°	29.5°±1°

TABLE III (contd.)

R_f values of coumarins in different solvents.

Coumarins \ Solvent No.	13.	14.	15.	16.	17.	18[d].	18[e].	19.	20.	21.
Ayapin	0.81	0.44	0.62	0.74	0.80	0 92	0.98	0.92	0.72	0.96
Bergapten	0.82	0.73	0.78	0.76	0 86	0.94	0.93	0.92	0 49	0.96
Byakangelicin	No spot	0.0	0.0	No spot	0.83	0.91	0 90	0.90	0.82	0.95
Coumarin	Do	No spot	No spot	Do	No spot	No spot	No spot	0.74	No spot	No spot
Ferulin	0.79	0.75	0.69	0.98	0.96	0.98	0.97	0.82	Do	0 95
Limettin	0.87	0.73	0.80	0.84	0.68	0.95	0.97	0.91	0.68	0.97
Luvangetin	0 93	0.68	0.79	0.88	0.69	0.96	0 97	0 93	0.82	0.95
Maremsin	0.90	0.06	0.08	0.88	0.85	0.92	0 97	0 91	0.87	0.96
Marmin	0.91	0.05	0.06	0.90	0 86	0.93	0.96	0.94	0.84	0.96
Murrayin	0.83	0.0	0.0	0.84	0.33	0.46	0.38	0.56	0.93	0 40
Pimpinellin	0.92	0.92	0.90	0.86	0.72	0.93	0 95	0.95	0.74	0.96
Seselin	0.92	0.93	0.90	0.84	0.74	0.93	0.95	0.95	0 74	0.97
Mixture	0.78	0.0	0.0	0.75	0.33[a]	0.44[c]	0.39[c]	Floures-	Continuous	0.39[c]
	0.85	0.74	0 08	0.80	0.62	0.92	0.93	cent zones	fluorescent	0.92
	0.93	0.92	0.80	0.85	0.74			overlapping.	zone.	
		0.98	0.91	0.91	0.86					
			0.93	0.99[b]	0.95[b]					
Expt. temp.	29 5°±1°	25.5°±.5°	27.5°±1°	29.5°±1°	28°±1°	30 5°±1°	30°± 5°	29.5°±1°	30°±1°	29.5°±1°

Remarks : a : bergapten, b : ferulin, c : murrayin ; d : ordinary ; e : borated.
Figs. 1, 2.....21 indicate the solvent systems mentioned in Table II.

In other solvents a similar situation was experienced with the mixtures. With some of the solvents, however, a few of the coumarins produced spots which were traced to a particular component of the mixture (vide Table III). These are bergapten, ferulin and murrayin.

TABLE IV

Colour produced by chromogenic spray.

	Ultraviolet fluorescence.			
	Untreated	NH_3 vapour.	2*N*-NaOH solution.	1% $KMnO_4$ solution.
Ayapin	v	br-b	b-g	g-y
Bergapten	yb	f-y	y	y-bn
Byakangelicin	bn	f-bn	l-bn	y-bn
Coumarin	...	q	gb	g-y
Ferulin	q-bn	deep bn (y*)	s (y*)	g-y
Limettin	vb	br-y	b	g-y
Luvangetin	yb	yb	br-y (y*)	g-y
Marmesin	vb	vb	l-b	y.bn
Marmin	vb	br-b	b	y-bn
Murrayin	vb	b	g-y	y-bn
Pimpinellin	pb	gb	y-g	g-y
Seselin	pb	gb	y-g	g-y

(f-faint, l-light, p-pale, br-bright, v-violet, vb-violetish blue, yb-yellowish blue, bn-brown, y-yellow, b-blue, gb-greenish blue, g-green, s-scarlet, q-quenching, * ordinary light)

DISCUSSION

It will be apparent from the results that incorporation of purely organic solvents to water enhances the R_f values of coumarins. Increase of R_f values of coumarins has also been noticed after addition of ammonia to water-pyridine system.

The addition of hydroxylic solvents (*n*-butanol, *iso*propanol) to water lowers the R_f values of murrayin, while incorporation of acetone or pyridine to water increases the same. When ammoniacal *iso*propanol is added to water, similar effect is observed. The lowering of R_f values has only been observed in the case of the glucoside, murrayin, by the use of borated paper. This result is consistent with the observations of Wachmeister (*Acta Chem. Scand.*, 1951, **5**, 976) and Swain (*loc. cit.*) that lowering of R_f values of coumarin glucosides may result due to chelation of the glucose residue with borate.

The behaviour of byakangelicin and ferulin, which are very close in their molecular structure, is interesting. Ferulin is $\gamma\gamma$-dimethyl-$\beta\gamma$-epoxyallyl ether of 8-hydroxy-5-methoxyfurano-2′ : 3′-6 : 7-coumarin, while byakangelicin is the corresponding dihydroxy compound. In water system ferulin shows no movement, while byakangelicin has R_f value of 0.54. In solvent system 14, byakangelicin does not move, while ferulin registers R_f value of 0.75.

It has been reported by Swain (*loc.cit.*) that spots of coumarin could only be detected in the ultraviolet light after spraying the developed chromatogram with 2*N*-sodium

hydroxide. In the present investigations spots of coumarin were observed without the use of spray reagents under ultraviolet light, when the solvent systems were pyridine-ammonia-water, formamide-ammonia-water, and *n*-butanol-acetic acid-water.

It appears from the present investigation that coumarins are to some extent separable and the most suitable solvent is water. Using water for this purpose, the R_f values were found to be generally less than 0.75. This supports, from theoretical considerations, the view that separation of coumarins by filter-paper chromatography probably involves factors other than pure liquid-liquid partition (Consden *et al.*, *Biochem. J.*, 1944, **38**, 224 ; Swain, *loc.cit.*).

The authors' thanks are due to Dr. D. M. Bose, Director, Bose Institute, for his keen interest in course of the work. Thanks are also due to Dr (Mrs.) A. Chatterjee of the University College of Science and Technology, Calcutta, for a gift of authentic specimens of some coumarins.

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ACTION OF NITROGEN TETROXIDE AND NITROGEN DIOXIDE ON ZINC CARBONATE (AND ZINC SULPHIDE)

By Vasantrai Trambaklal Oza

Action of nitrogen tetroxide and dioxide and their thermal dissociation products on zinc carbonate has been investigated and nitrogen tetroxide has been found to react almost immediately in contact with zinc carbonate.

Action of nitrogen tetroxide and its thermal dissociation products on metallic zinc and zinc oxide has been investigated by Addison, Lewis and Thompson (*J. Chem. Soc.*, 1951, 2829), and on anhydrous sodium carbonate by Addison and Lewis (*ibid.*, 1953, 1319). Calcium carbonate, when treated with nitrogen tetroxide or dioxide, is supposed to give only calcium nitrate (Briner, Lugrin and Monnier, *Helv. Chim. Acta*, 1930, **13**, 64). No further work is reported in the literature.

The author, while studying the reactions of nitrogen tetroxide and its thermal dissociation products on oxides and nitrite , found that nitrogen tetroxide reacted almost immediately on contact with zinc oxide in accordance with the observations made by Addison *et al.* (*loc. cit.*). Zinc sulphide, identical in structure with zinc oxide, was also found to react instantaneously with nitrogen tetroxide and dioxide mixture. Some of the products of reaction were analysed and found to contain zinc nitrate as one of the products of reaction, but the whole system was found to be complicated. The reaction with zinc carbonate, which did not seem to be much complicated, has been thoroughly investigated in this paper.

Experimental

Zinc carbonate used was extrapure A. R. chemical and its purity was established before working. Nitrogen tetroxide was prepared after Oza, Oza and Thaker (*J. Chem. Soc.*, 1955, 2457).

Liquid N_2O_4 *system.*—Pure nitrogen tetroxide was condensed and filled in reservoir R (Fig. 1). The compound to be treated with liquid N_2O_4 was weighed in a small tube, d (diameter about 3 mm.) as shown in Fig. 2a. This was then drawn out by heating so as to convert it into a form of the type as shown in Fig. 2b. Proper care was taken to see that no compound stuck on the wall of the glass tube. This was then sealed up at Z (Fig. 1). The tube (d) with the substances in this position was then surrounded with a bath containing a freezing mixture (common salt + ice) at -10° to -15°, and maintained there for about 15 minutes. X was then opened and liquid N_2O_4 was allowed to be distilled rapidly in the tube. A slight reaction took place on contact of N_2O_4 with the substance, turning the colour of N_2O_4 slightly green (due to the formation of N_2O_3,) but the N_2O_3, thus formed, remained adsorbed on the substance because of the low temperature. More N_2O_4 was allowed to be collected over the substance till the

tube was about 2/3 filled. The liquid N_2O_4, collected over the substance, retained its characteristic yellow colour, thus showing that N_2O_3, slightly formed, remained adsorbed on the substance only. In case the colour of N_2O_4 over the substance was found to turn green, the experiment was rejected. R was then cooled by a bath of ice and water ; tap X was closed and the lower part of the tube was removed by sealing at its capillary end. The sealed tube was then brought to 20° to 25°, and within a few minutes the substance reacted and the yellowish viscous liquid appeared in the tube in place of the white solid powder. The colour of the liquid (N_2O_4) turned greenish blue.

FIG 1

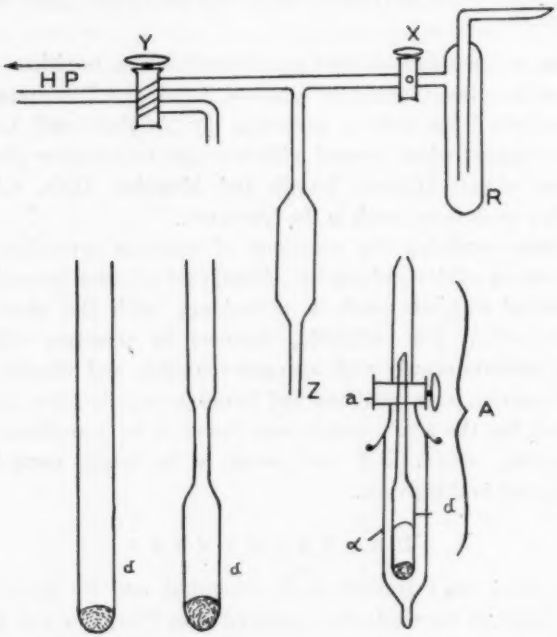

FIG. 2a. FIG. 2b. FIG. 3.

Interesting observation was met with when the experiment was carried out with zinc sulphide (0.123 g. taken in tube d). Liquid N_2O_4 was allowed to be poured on the substance in the same manner as mentioned above with zinc carbonate. But on bringing the substance at room temperature, the reaction was found to be vigorous, showing the appearance of boiling of N_2O_4, which turned greenish blue ; the tube then burst out with explosive violence. The gases evolved after explosion smelt of sulphur dioxide or sulphur trioxide. The solid residue contained at least zinc nitrate and zinc sulphide among the products. The reaction could be controlled if much smaller amount of zinc sulphide were used.

The tubes 'd' containing viscous liquid and condensed gases were allowed to remain at constant temperatures (22° to 25°) for hours and days.

The action of nitrogen dioxide on zinc carbonate was studied by the same method and apparatus as used by Oza, Oza and Thaker (Fig. 1, *J. Chem. Soc.*, 1955, 2457).

Products of Reaction.—The tube 'd' containing all the products of reaction, kept for hours, was now taken for analysis. This tube was carefully cleansed and weighed. It was then inserted in another tube α (Fig. 3) having a detachable ground-glass joint. The tube 'd' was placed in such a way that when α was fixed to A (as shown in Fig. 3), its capillary portion passed through the bore of the key of the tap, as shown in Fig. 3. This whole part A was then joined to the main system, as shown in Fig. 1 [Oza, Oza and Thaker, *loc. cit.*] by means of its ground-glass joint. The apparatus was evacuated, 'b'' was closed, and dry air was introduced in the system ; a strong potash lye was filled in C, D and E, and again the apparatus was evacuated. The capillary end of the tube 'd' was then broken and the gaseous products were cooled in P. 'b'' was then opened and the nitrous fumes were allowed to be absorbed in alkali*. When the apparatus was clear of the nitrous fumes, dry air was introduced in the system by breaking the capillary end of α. 'd' was removed quickly and sealed. The broken pieces were also removed and collected, washed with dry ether and weighed along with 'd'. Solutions in alkali bulbs were mixed and made to a known volume and analysed for nitrite and nitrate ; from these results the amounts of N_2O_3 and N_2O_4 in the gaseous mixture were calculated. It was difficult to analyse carbonate in presence of nitrite, but its analysis was not necessary. The tube 'd', now containing the viscous product only, was weighed and placed in α, as done before, and the system was evacuated. Alkali was then filled in C, D and E, taking necessary precautions. The tube 'd' was again broken at its capillary end. The tube was now surrounded by a heating contrivance and temperature was raised slowly to 100°. The heating was continued till the yellow viscous liquid changed to a white powder, and no more bubbles escaped in alkali bulbs. The tube 'd' along with its broken pieces was removed as usual and weighed. The residue was dissolved out in water. Almost a negligible amount of the substance was left insoluble. The water-soluble portion was analysed for nitrite and nitrate, and only nitrate was formed. The solution in the alkali bulb was analysed for nitrite and nitrate, and as usual calculations were made for N_2O_3 and N_2O_4.

In the gaseous system zinc carbonate was allowed to react with nitrogen dioxide for one hour at different temperatures. The bath was maintained at the temperature of experiment till all the nitrous fumes from the system were absorbed in alkali. The residue at the end of the experiment was quickly weighed and dry carbon tetrachloride was added to the residue to remove the adsorbed nitrous fumes, and the carbon tetrachloride solution containing dissolved nitrous fumes was poured on alkali solution (about 1 *N*) and shaken vigorously. The aqueous portion was examined for nitrite and nitrate contents. The residue after treatment with carbon tetrachloride was dried and dissolved in water. The soluble portion was made to a known volume through filtration. The insoluble residue was analysed for unchanged zinc carbonate by determining its zinc content volumetrically by standard $K_4Fe(CN)_6$. Carbon dioxide was calculated from zinc carbonate used up.

* The notations used refer to Fig. 1 of Oza *et al.* (*loc. cit.*).

TABLE I

Action of nitrogen tetroxide on zinc carbonate.

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Expt. No.	Period of contact,	$ZnCO_3$.	N_2O_4 found.	Wt. of V.P.	Decomp. of V.P.		N_2O_4 left.	N_2O_4 consumed	N_2O_3 formed.	CO_2 calc.	Approx. ratio.		
					$Zn(NO_3)_2$.	N_2O_4.					9:3.	7:6.	10:11.
1	6 hours	0.0204 g.	0.3251 g.	0.0627 g.	0.0309 g.	0.0298 g.	0.2637 g.	0.0614 g.	0.01335 g.	0.00716 g.	4	2	1
		* (1.627	(35.33	(1.68	(1.63	3.24	(28.82	(6.66	(1.73	(1.62			
		$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)			
2	24 hours	0.035	0.400	0.1000	0.05364	0.0525	0.2850	0.115	0.02087	0.0123	4.4	2	1
		(2.79	(43.5	(2.7	(2.81	(5.695	(30.9	(12.5	(2.74	(2.79			
		$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)			
3	7 days	0.0457	0.3752	0.1401	0.0708	0.0657	0.243	0.1322	0.02666	0.01603	4	2	1
		(3.644	(40.77	3.75	(3.68	(7.12	(26.2	(14.3	(3.5	(3.644			
		$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)			
4	1 month	0.0505	0.389	0.1584	0.0772	0.0739	0.2462	0.1428	0.0315	0.1772	4	2	1
		(4.04	(43.3	(4.24	(4.04	(8.04	(26.7	(15.5	(4.14	(4.02			
		$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)			
5	2 months	0.025	0.396	0.0784	0.0386	0.03561	0.3138	0.0776	0.01737	0.00877	4.4	2	1
		(1.992	(43.4	(2.1	(1.996	3.87	(34 0	8.4	(2.24	(1.992			
		$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)	$\times 10^{-4}$)			

* Gram molecular quantities are shown in parenthesis. V.P. denotes viscous product.

TABLE II

Action of nitrogen dioxide on zinc carbonate

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
					Residue found		$ZnCO_3$ used up.	Adsorbed gases.		N_2O_4 left.	N_2O_4 used up.	N_2O_3 formed.	CO_2 (calc.)	Approx. ratio.	
Expt. No.	Temp	$ZnCO_3$ taken.	N_2O_4 taken.	Residue formed.	$Zn(NO_3)_2$.	$ZnCO_3$.		N_2O_4.	N_2O_3.					8:12.	13:14.
1	2°	0.1000 g.	0.1904 g.	0.144 g.	0.07892 g. (4.17×10⁻⁴)	0.050 g.	0.050 g. (3.97×10⁻⁴)	0.00797 g.	...	0.1084 g.	0.0741 g. (8.05×10⁻⁴)	0.03054 g (4.03×10⁻⁴)	0.01718 g. (3.978×10⁻⁴)	2	1
2	10°	0.1034	0.2535	0.1795	0.1384 (7.31×10⁻⁴)	0.01081	0.0926 (7.36×10⁻⁴)	0.02136	0.001g.	0.0918 g.	0.1404 (15.27×10⁻⁴)	0.05175 (7.17×10⁻⁴)	0.0326 (7.41×10⁻⁴)	2	1
3	60°	0.100	0.161	0.142	0.0987 (5.21×10⁻⁴)	0.03546	0.06454 (5.14×10⁻⁴)	...	...	0.07065	0.09035 (9.82×10⁻⁴)	0.038 (5.0×10⁻⁴)	0.02852 5.15×10⁻⁴)	2	1
4	80°	0.105	0.167	0.1401	0.09112 (4.81×10⁻⁴)	0.04705	0.05795 (4.62×10⁻⁴)	...	...	0.0828	0.0842 (9.15×10⁻⁴)	0.03563 (4.69×10⁻⁴)	0.02033 (4.62×10⁻⁴)	2	1
5	100°	0.1034	0 166	...	0.1010 (5.33×10⁻⁴)	0.0404	0.063 (5.02×10⁻⁴)	...	...	0.0682	0.0978 (10.6×10⁻⁴)	0.0382 (5.03×10⁻⁴)	0.02208 (5.02×10⁻⁴)	2	1

The gram molecular quantities are shown in parenthesis.

Discussion

As seen from Table I, the quantities of nitrogen tetroxide and zinc carbonate used up are in the ratio of 4 : 1 ; the reaction with zinc carbonate in liquid system thus appears to proceed according to the equation,

$$ZnCO_3 + 4N_2O_4 \rightarrow Zn(NO_3)_2.2N_2O_4 + N_2O_3 + CO_2 \quad \ldots (a)$$

That the reaction is running exactly in this manner is further supported by the formation of N_2O_3 and CO_2 in equimolecular quantities. Viscous product must be a compound having the formula, $Zn(NO_3)_2.2N_2O_4$, as has been proved from the results of its decomposition.

$$Zn(NO_3)_2.2N_2O_4 \rightarrow Zn(NO_3)_2 + 2N_2O_4 \quad \ldots (b)$$

The ratio obtained in column (13) is in accordance with the above equation. The reaction in the gaseous system is found to proceed according to

$$ZnCO_3 + 2N_2O_4 \rightarrow Zn(NO_3)_2 + N_2O_3 + CO_2 \quad \ldots (c)$$

followed by rapid absorption of NO_2 by zinc nitrate formed, so as to form the yellow viscous complex.

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ALTERNATING CURRENT ELECTROLYSIS. PART VII. OSCILLOGRAPHIC STUDY OF POTENTIAL VARIATIONS AT A PLATINUM ELECTRODE IN SULPHURIC ACID

By K. M. Joshi

A study of current-voltage characteristics and voltage-time curves during A. C. electrolysis has been presented. The voltage-time curves obtained show that during the anodic half-cycle, the processes taking place are (*i*) desorption and ionisation of previously adsorbed hydrogen, (*ii*) charging of electrode double layer and (*iii*) the formation of a film of PtO of one molecule thickness leading to the steady evolution of oxygen. The cathodic half-cycle consists of several stages, representing the (*a*) charging of double layer, (*b*) the reduction of oxide and (*c*) formation of a monatomic layer of hydrogen atoms on the electrode leading to a steady oxygen evolution. At higher frequencies of alternation, the potential does not reach the value corresponding to the hydrogen or oxygen evolution value.

Chemical effects produced by symmetrical alternating current between platinum electrodes in sulphuric acid solutions have been reported in a previous investigation (Part III, this *Journal*, 1954, **31**, 278). If during A. C. electrolysis, the polarised platinum electrode and a stationary reversible electrode, kept in the same solutions, are connected to the Y-plates of an oscillograph, using time base, the trace obtained on the screen will represent voltage-time relation at the electrode during an entire cycle. A study of these curves as well as current-voltage characteristics of an electrode during A. C. electrolysis is presented in this communication.

Bowden (*Proc. Roy. Soc.*, 1929, **125 A**, 446) found an almost linear relation between electrode voltage and quantity of electricity passed when a platinum electrode was changed from cathodic to anodic polarisation. In addition, some arrests were observed on the curve which were attributed to the depolarisation of hydrogen and reduction of platinum oxide during the anodic and cathodic voltage build-up respectively. The anodic process was found to be the removal of adsorbed hydrogen and the formation of an adsorbed layer of oxygen atoms. Butler and Armstrong (*ibid.*, 1932, **137A**, 604) observed that prior to the evolution of oxygen, entire surface of the electrode was covered with an envelope of oxygen atoms. These workers further reported that the initial process, when a hydrogen-evolving electrode was changed to oxygen-evolving one, was the ionisation of adsorbed hydrogen (*J. Chem. Soc.*, 1934, 743). Pearson and Butler (*Trans. Faraday Soc.*, 1938, **34**, 1163) detected three stages during anodic polarisation of platinum eloctrode, considered to be due to: (1) removal of adsorbed hydrogen, (2) charging of electrode double layer, and (3) deposition of monatomic layer of oxygen leading to a steady oxygen evolution. The cathodic polarisation curve also contained the same three stages. Hickling (*ibid.*, 1945, **41**, 333) confirmed these observations. However, Hickling suggests that before a steady evolution of oxygen can occur, adsorption of oxygen dipoles on the electrode leading to the formation of platinum oxide may occur.

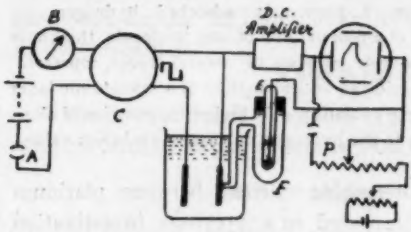
Thus, from the literature we find that the steady evolution of oxygen or hydrogen at a platinum electrode is preceded by several other processes. Since, in the present

case, an electrode is subjected to A. C. polarisation, a study of voltage-time curves will provide an idea of the different processes taking place when an electrode, evolving oxygen, is changed to hydrogen-evolving one, and *vice versa*.

EXPERIMENTAL

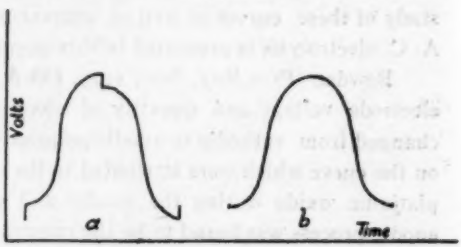
The experimental arrangement used is shown in Fig. 1. The polarising current was taken from circuit ABC where C was the rotating commutator. The A. C. was fed to two polished platinum electrodes dipping in H_2SO_4 solution. E was standard half cell- Hg/Hg_2SO_4-$M/2$ K_2SO_4 -placed in a vessel F containing $M/2$-K_2SO_4 and contact with the electrode was made through a Luggin capillary. The voltage between the platinum electrode and reference electrode was fed through D. C. amplifiers to the Y-plates of a cathode ray oscillograph. The Y-deflection on the screen was calibrated by means of the potentiometer P.

FIG. 1



The oscillograms were photographed with a Du Mont camera ; the O-voltage trace as well as the oscillograph screen was also photographed on the same film for reference.

FIG. 2



Luggin Capillary Adjustment.—It was found that as the capillary tip was moved away from the electrode, the peak to peak voltage of the trace appearing on the C.R.O. screen increased. The capillary tip was therefore pushed towards the electrode till the peak to peak voltage was minimum and there was no voltage drop at the cut off taking place between the positive and negative half-cycles. This is shown in Fig. 2(*a*) which shows the trace when the capillary tip is slightly away from the electrode surface. Fig. 2(*b*) shows the change in the wave-form when the tip is touching the electrode. To decrease the IR drop between the capillary tip and the electrode, K_2SO_4 was added to the electrolyte so that it was $M/2$ with respect to K_2SO_4.

Current-voltage measurements were done by gradually increasing the current, the peak to peak voltage being measured on the calibrated oscillograph screen as the trace appeared on it. The position of the O-voltage trace being known, the peak voltage above this line affords the maximum potential during the cathodic cycle and below it gives the maximum potential during the anodic cycle. Knowing the potential of the half cell, the maximum anodic and cathodic potential during the entire cycle can be calculated. These results are plotted at different values of frequency of alternation (Figs. 3 and 4). All the voltages recorded are on hydrogen scale.

FIG. 3

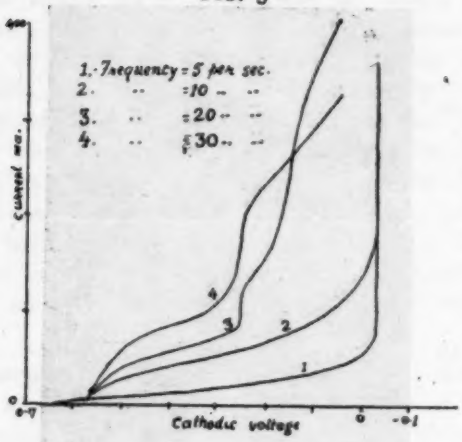
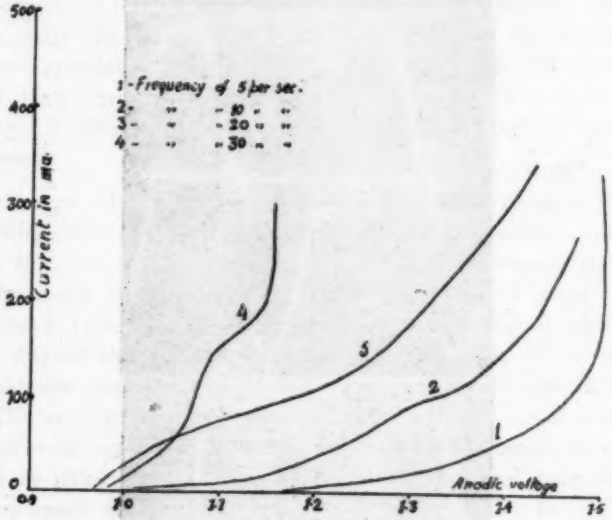


FIG. 4



DISCUSSION

Potential-time Curves.—As the current is increased, the potential-time wave-form as appears on the C.R.O. screen also varies. At lower values of current strength, the wave-form is logarithmic in each half-cycle (Fig. 5*a*). On increasing the current, the wave-form has the shape shown in Fig. 5*b*. At this stage, it will be seen that the voltage during cathodic half-cycle abruptly falls to a value of +0.65 v, then slowly becomes more negative, then rapidly falls linearly with time. The anodic half-cycle also shows a rapid rise of potential to a value of +0.65 v. Beyond this value, the voltage rises linearly with time. On increasing the current

Fig. 5a.

Fig. 5b.

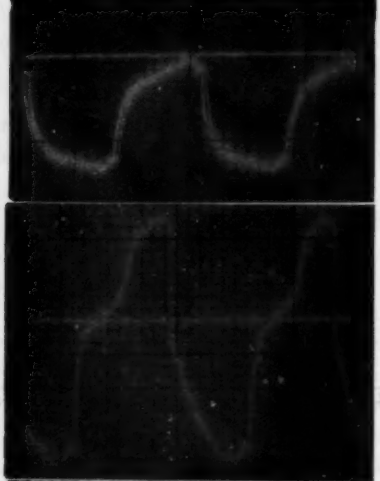


Fig. 5c.

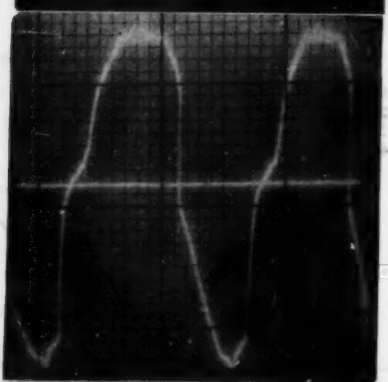
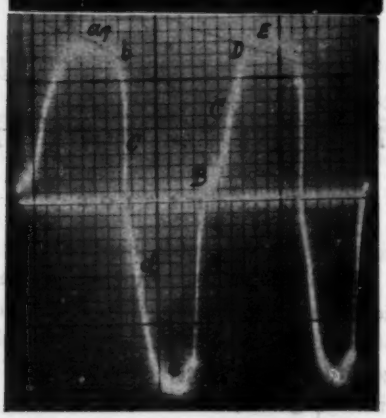


Fig. 5d.



further (Fig. 5*c*), the anodic curve is seen to rise slowly in the initial stages, then rapidly to a value of 0.85 v; the cathodic curve also shows a similar kink at a voltage of +0.35 v. At a still higher current strength, the curve shape is nearly retained, but the anodic curve is seen to flatten out; there is a similar flattening observed in the cathodic curve also (Fig. 5*d*). This stage corresponds to visible gas evolution at the electrode and the maximum negative potential (peak value) during cathodic cycle is -0.03 v, which corresponds to the hydrogen overvoltage value at platinum. Beyond this stage, increase in current strength increases the length of the flat top in both the half-cycles. It is significant to note that during the anodic voltage build-up, the voltage continues to be that of hydrogen evolution value during the first few microseconds. Such a behaviour is not obtained during cathode voltage build-up.

From an examination of the current-voltage curves, it can be seen that during cathodic discharge, at low frequencies, the voltage rises slowly at first, then rapidly and finally reaches a constant value corresponding to hydrogen evolution. This curve is very much similar to the C×V curves obtained in D. C. electrolysis except for the slow rise of potential in the initial stages. At higher frequencies, the shape of the curve is essentially the same except for the fact that the initial slow rise of potential is more prominent and the voltage does not reach the hydrogen evolution value even at high current strength. At higher frequencies, a break at a voltage value of +0.25 v is obtained. The anodic curve shows a break at +1.07 v at higher values of frequency.

An examination of the voltage-time curves, obtained at a stage when gas evolution is taking place at the electrode, shows that the anodic curve contains five distinct stages (Fig. 5*d*). The initial stages 'a' and 'b' are obviously due to the presence of adsorbed hydrogen on the electrode since the potential at 'a' corresponds to the H-overvoltage value. The stage 'b', where the potential rises linearly with time, may be due to the ionisation of adsorbed hydrogen. These stages have been reported by Pearson and Butler (*loc. cit.*). The number of coulombs contained in stages 'a' and 'b' are 120 and 300 microcoulombs per sq. cm. of electrode surface. The total number of coulombs contained in both these stages corresponds to the value, reported by Hickling (*loc. cit.*), for the desorption and ionisation of adsorbed hydrogen during anode voltage build-up. The stage 'c' is due to the charging of the double layer as the length of this stage has not been found to be affected by electrode poisons. This is further substantiated by the fact that the potential of a static platinum electrode in the same electrolyte is the same as that obtained at the end of the stage 'c'.

The stage 'd' commences at a potential of +0.82 v. The potential of Pt/PtO in $2N$-H_2SO_4 has been shown by Grube to be 0.9 v (*Z. Elektrochem.*, 1910, **16**, 621). Hence, it is likely that this stage may be due to the commencement of the formation of an oxide layer on the electrode. This stage is found to contain 900 microcoulombs per apparent sq. cm. of electrode surface. These would liberate 1.4×10^{15} molecules or 2.8×10^{15} atoms of oxygen. Since there are approximately 1.6×10^{15} atoms of platinum per sq. cm.

of electrode surface and as the true area can be considered to be about twice the apparent area, this stage corresponds to the formation of a monatomic layer of oxygen atoms, completely covering the electrode surface. Alternatively, it can be assumed that the formation of PtO takes place at the electrode during this stage, the thickness of the oxide layer being of one molecule. The voltage build-up curve during the cathodic half-cycle shows a break at a voltage corresponding to the reduction of PtO formed previously. However, it is observed that the anode voltage build-up curve does not 'stay' at the voltage corresponding to the formation of the oxide ; on the contrary, the voltage rises linearly with time. Hickling (*loc. cit.*) suggests the adsorption of oxygen dipoles on the electrode resulting in the formation of an unstable 'species' reacting rapidly to form PtO.

The cathodic voltage build-up curve consists of an initial stage 'A' corresponding to the charging of electrode double layer. It is significant to note that the lengths of this stage and the anodic stage 'c' are the same. This stage is followed by stage 'B' during which the voltage 'stays' at a voltage of +0.65 v. This stage is found to contain 500 microcoulombs. The stage is therefore probably due to the presence of PtO on the electrode surface, the reduction of the oxide taking place at a more negative potential than that required for its formation. After this stage the potential again rises rapidly till the deposition of hydrogen atoms takes place. This stage 'C' contains 500 microcoulombs which results in the deposition of 3.2×10^{15} atoms of hydrogen on the electrode surface. Taking into account the fact that some of the hydrogen may diffuse into the metal, it is apparent that the steady evolution of hydrogen is preceded by the formation of an envelope of hydrogen atoms on the electrode. This is in confirmity with the observations of previous workers (*loc. cit.*).

The author wishes to express his indebtedness to Dr. A. N. Kappanna for advice and helpful suggestions during this work.

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A NOTE ON *m*-BROMOPHENYLTHIOUREA AND ITS MERCURATED DERIVATIVES

By G. N. Mahapatra

Although the synthesis and the properties of *o*- and *p*-bromophenylthioureas have been described in the literature (Dyson *et al.*, *J. Chem. Soc.*, 1927, 436; 1924, **125**, 1702; Shimotani, *J. Pharm. Soc. Japan*, 1952, **72**, 328), the preparation of *m*-bromo analogue does not appear to have been previously recorded. The *m*-bromophenylthiourea has now been synthesied by heating *m*-bromoaniline hydrochloride with ammonium sulphocyanide in aqueous medium.

In view of the possible fungicidal action of thiourea (Horsfall, "Fungicides and their action"; *Chronica Botanica Co.* 1945, p. 126) and N-substituted monoarylthioureas (Shimotani, *J. Pharm. Soc. Japan*, 1952, **72**, 919) and the commercial use of mercurated thiourea as fungicide under the trade name of 'Lunasan' (McCallan *et al.*, *Phytopath.*, 1955, **45**, 299), the synthesis of mercurated derivatives of the above thiourea has been undertaken with the expectation that they may show promising fungicidal activity.

The *m*-bromophenylthiourea has been mercurated using mercuric acetate to afford an acetoxymercuri compound. On the basis of earlier observations on the mercuration of aromatic amines (Newton Friend, "Text-book of Inorganic Chemistry", Vol. XI, 1928, Part I) and arylthioureas (Guha Sircar and Patnaik, this *Journal*, 1950, **27**, 535), it has been assumed that the acetoxymercuri group enters the aryl nucleus at the *para* position (with respect to -NH group).

This acetoxymercuri compound has been converted into chloro- and bromomercuri compounds since a few of the chloromercuri compounds had been found earlier to be more effective than the corresponding acetoxymercuri derivatives.

The chloromercuri compound has been prepared by Bruice's method (*J. Amer. Chem. Soc.*, 1950, **72**, 593), by adding sodium chloride to the reaction mixture from which the acetoxymercuri compound is to be isolated.

The bromomercuri compound has been prepared in a similar way, by adding a concentrated solution of KBr to the reaction mixture from which the acetoxymercuri compound is to be isolated.

m-*Bromophenylthiourea.*—*m*-Bromoaniline (8.6 g.) and HCl (conc., 8 c.c.) were taken in a conical flask and water (60-80 c.c.) was added to dissolve the hydrochloride on heating. NH_4SCN (7 g.) was added to the hydrochloride solution and the whole mixture was refluxed on a boiling water-bath for 2 to 3 hours, when a white precipitate appeared. It was collected by filtration and recrystallised from dilute alcohol in white, glistening, light-weight plates, m.p. 138°, yield 80%. It is soluble in alcohol and bitter in taste. (Found: Br, 34.81; S, 13.53. Calc. Br, 34.63; S, 13.85 per cent).

p-*Acetoxymercuri*-m-*bromophenylthiourea*.—*m*-Bromophenylthiourea (2 g.) was dissolved in alcohol-dilute acetic acid solution and was treated with an aqueous solution of mercuric acetate (2.8 g. in 40 c.c. water), acidified with acetic acid. There was immediate precipitation. The reaction mixture was kept overnight. The precipitate was collected and washed thoroughly with hot water and finally with alcohol and very dilute acetic acid, m.p. 275-76°, yield 75%. (Found: Hg, 40.13. Calc. Hg, 40.89 per cent).

p-*Chloromercuri*-m-*bromophenylthiourea*.—Acetic acid (4.8 g.) was treated with $NaHCO_3$ (2.5 g.) and diluted with 30 c.c. of water (p_H 4.3) and to that mercuric acetate (3.2 g.) was added, followed by *m*-bromophenylthiourea (1 g.), dissolved in alcohol and dilute acetic acid. On addition of a concentrated solution of sodium chloride (2.5 g. in 10 c.c. water) to the above mixture, a white precipitate appeared. The reaction mixture was set aside for 24 hours. It was then filtered and washed thoroughly with hot water, followed by alcohol, m.p. $>350°$, yield 70%. (Found: Hg, 41.98. Calc. Hg, 42.96 per cent).

p-*Bromomercuri*-m-*bromophenylthiourea*.—The method was exactly the same as above excepting that KBr solution was employed in place of NaCl; m.p. $>350°$, yield 65%. (Found: Hg, 39.69. Calc. Hg, 39.21 per cent).

Bactericidal Test.—The Rideal-Walker serial drop dilution method was used for assaying the antibacterial action of the acetoxy-, chloro- and bromo-mercuri compounds. The test organisims were 24 hours' culture of *E. coli* and *Staphylococcus aureus*. The acetoxy- and chloro- and bromo-mercuri compounds were found to be active in dilutions 1 : 80,000, 1 : 100,000 and 1 : 100,000 respectively.

Fungicidal Test.—For assaying the fungicidal activity, the method of Montgomery and Moore (*J. Pomol. Hort. Sci.*, 1938, **15**, 253) with a slight modification was used. *Piricularia orizae*, Cav., the causative organism of the blast of rice, was used as the test fungus. The mercurated compounds were found to possess good fungicidal activity, the percentage inhibition of spore germination being cent per cent at 100 p.p.m in case of *m*-(bromophenylthiourea) and 4-5 p.p.m with the acetoxy-, chloro- and bromo-mercuri compounds.

The author is particularly grateful to Dr. S. S. Guha Sircar, formerly Professor of Chemistry, Ravenshaw College, Cuttack, for his kind advice and to Mr. S. Y. Padmanavan, the Mycologist of the Central Rice Research Institute, Cuttack for supplying the test fungus to carry out the fungicidal work in this laboratory.

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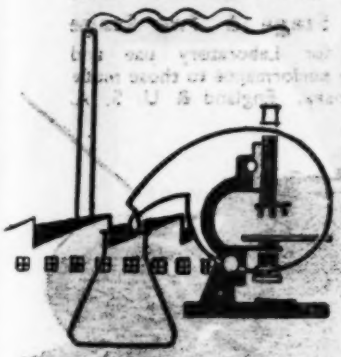

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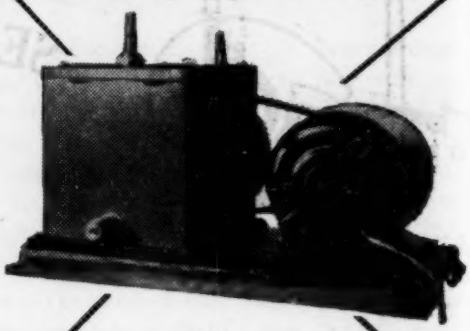

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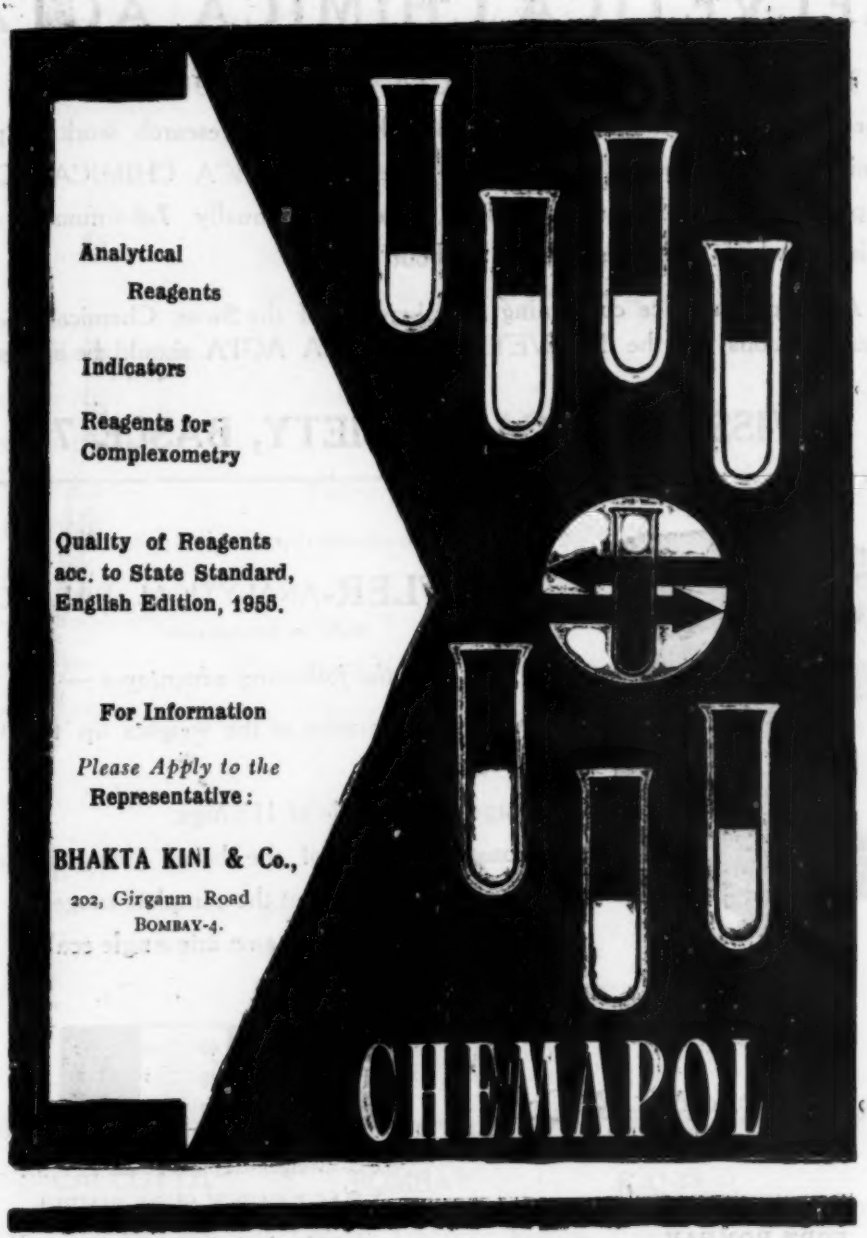

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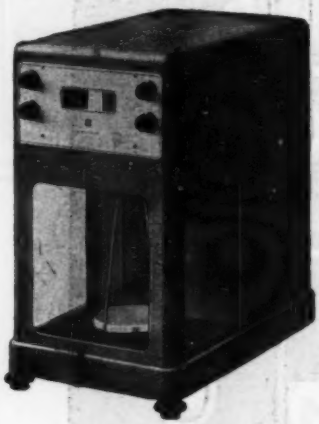

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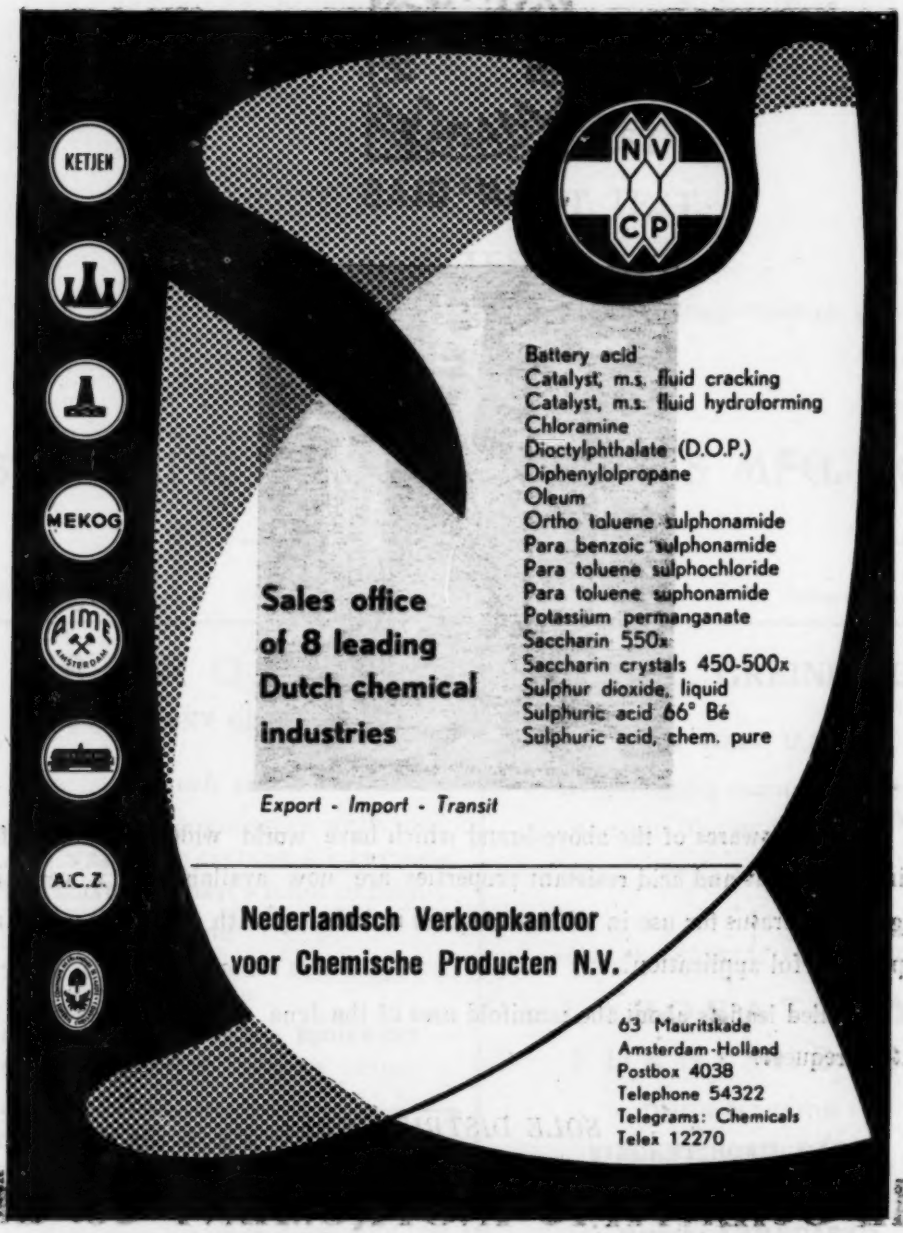
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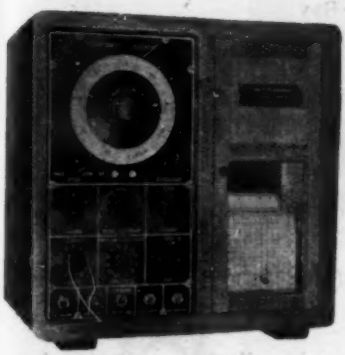

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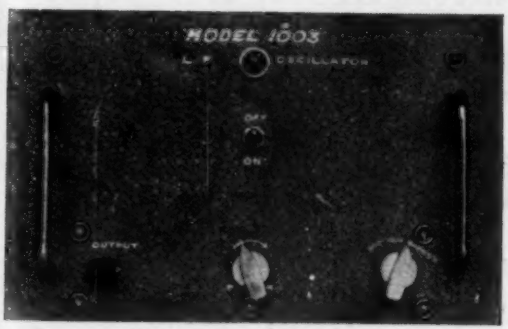

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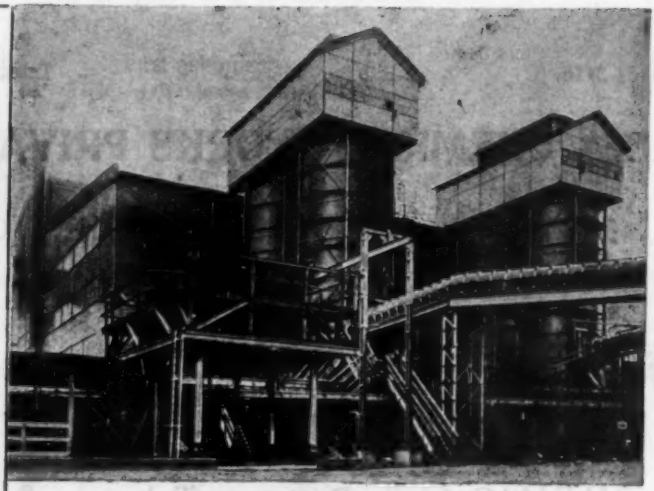

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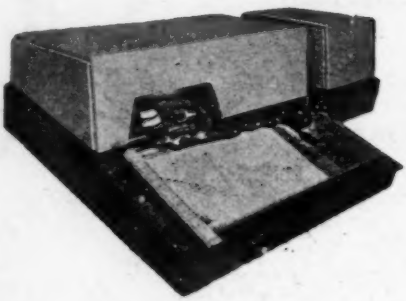

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Page.	Line.	*Read*	*for*
58	4	as the electrode *after* "slowed down".	
60	last line	$2H+SO_4^{2-} \rightarrow$	H_2SO_4+2e for eq. 6
144	Table II, column 2, line 2	'*m*' *before* toluidide	
291	Table I, last colum last line	'3' to be elivated to the next upper line	
294	21	alkyl-	alcekalyl-
	25	model	modal
476	Fig. 1	*density*	*densiiy*

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